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THE USE OF GLASS ION-SELECTIVE ELECTRODES FOR THERMODYNAMIC STUDIES ON ELECTROLYTE SOLUTIONS 1:1 IN WATER–ORGANIC SOLVENT SYSTEMS.
STUDIES IN THE WATER–THF SYSTEM

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ABSTRACT

The EMF of the cell glass electrode (Na)|NaCl|AgCl,Ag in water–tetrahydrofuran (THF) mixtures containing 0, 2.5, 7.5, 10, 15, 20, 25, 30 mol% THF has been measured within the temperature range 293.15–308.15 K. Standard EMF and thermodynamic functions of transfer of NaCl ($\Delta G_t^{\ominus}$, $-T\Delta S_t^{\ominus}$, $\Delta H_t^{\ominus}$) from water to water–THF mixtures were also determined. The values obtained have been compared with the corresponding values obtained by other authors.

The possibilities of using cation-selective glass electrodes for thermodynamic studies on electrolyte solutions in systems containing aprotic solvents–water mixtures are evaluated including a critical review of the opinions of other authors.

INTRODUCTION

Extensive controversy and very different opinions on the applicability of glass ion-selective electrodes for thermodynamic studies on electrolyte solutions in aqueous–organic systems have brought the authors to undertake a course of studies on this subject [1–4]. Thus, for instance, Juillard and other authors [5–13] have used glass ion-selective electrodes to determine the free enthalpy of transfer of electrolyte from water to various mixed solvents. On the other hand, other authors disagree with the suitability of such a procedure [14,15]. It is also thought that the applicability of glass ion-selective electrode in a mixed solvent is restricted to systems containing less than 30 wt.% of organic cosolvent [16–18]. A detailed review of the above-mentioned opinions is reported in ref. 19.

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Most of the controversy concerns the applicability of a glass sodium electrode in mixtures of aprotic solvent and water. The results of our previous studies using water–alcohol systems (within a wide temperature range) [1–3] and water–DMF systems (at 298.215 K) [4] have encouraged us to verify the applicability of glass ion-selective electrodes for thermodynamic studies in other systems, mainly in aprotic solvents.

NaCl in water–tetrahydrofuran (THF) systems was selected for examination with the glass sodium electrode for two reasons: (1) THF is an aprotic solvent, and (2) the NaCl–water–THF system has been insufficiently examined. The EMF of the cell glass electrode (Na) | NaCl | AgCl,Ag in water–THF systems was measured for various THF contents up to 30 mol%. The authors are aware that at higher THF contents there is a greater possibility of committing errors if one does not take into account ionic association.

EMF measurements of the above cell were carried out at several temperatures. The examination resulted in more complete thermodynamic characteristics and consequently results than those of other authors; this has allowed the applicability of the glass sodium electrode for such studies to be evaluated better.

It should be noted that there is a lack of literature reports on the temperature coefficients of the EMF of cells using glass electrodes.

EXPERIMENTAL

NaCl (AnalaR grade, Polish Chemical, Poland) was crystallised twice from redistilled water and dried under vacuum at 335 K.

Tetrahydrofuran (Loba Chemie) was purified according to the procedure reported in ref. 20.

Water was distilled twice from a basic $KMnO_4$ solution, rejecting a considerable part of the first run.

The method and apparatus for measurements were described in detail in previous papers [1–4].

RESULTS AND DISCUSSION

The EMF of the cell glass electrode (Na) | NaCl | AgCl,Ag was measured at temperatures of 293.15–318.15 K, using NaCl solutions with a concentration of 0.01–0.08 mol kg^{-1} of solvent, the THF content varying from 0 to 30 mol% (0–34% by weight). The values of the standard EMF ($E^{\ominus}$) were obtained by linear extrapolation to $m = 0$ of the following function:

$$\begin{aligned} f(m) &= E + 2\theta \ln m - 2\theta \frac{A(d_0 m)^{1/2}}{1 + RB(d_0 m)^{1/2}} - 2\theta \ln(1 + 0.002mM) \\ &= E^{\ominus} - 2\theta Cm \end{aligned} \qquad (1)$$

TABLE 1

Standard EMFs of the cell glass electrode (Na) | NaCl | AgCl,Ag in water–THF mixtures

THF (mol%)	$E^{\ominus}$ (V)					
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0	−0.1229	−0.1245	−0.1264	−0.1284	−0.1303	−0.1323
1.0	−0.1294	−0.1312	−0.1331	−0.1349	−0.1368	−0.1388
2.5	−0.1397	−0.1414	−0.1433	−0.1454	−0.1474	−0.1494
5.0	−0.1537	−0.1556	−0.1576	−0.1598	−0.1618	−0.1641
7.5	−0.1641	−0.1661	−0.1681	−0.1701	−0.1723	−0.1745
10.0	−0.1788	−0.1808	−0.1829	−0.1850	−0.1872	−0.1896
15.0	−0.2041	−0.2062	−0.2086	−0.2109	−0.2135	−0.2163
20.0	−0.2237	−0.2260	−0.2284	−0.2308	−0.2331	−0.2355
25.0	−0.2458	−0.2484	−0.2508	−0.2536	−0.2558	−0.2584
30.0	−0.2656	−0.2691	−0.2718	−0.2747	−0.2776	−0.2805

where E is the measured EMF, $\theta = 8.3143T/F$ (V), T is the temperature (K), F is the Faraday constant (C mol^{-1}), d_0 is the solvent density, M is the molar mass of the solvent (g mol^{-1}), R is the distance parameter of the ions (Å),

$$A = \frac{1.8246 \times 10^6}{(\epsilon T)^{3/2}} \times \ln 10$$

$$B = \frac{50.29}{(\epsilon T)^{1/2}}$$

and ϵ is the relative permittivity of the solvent.

The values of the electric permittivity and solvent density necessary for the calculations were obtained by interpolation of the data contained in refs. 21 and 22.

According to the suggestions of Justice [23,24], it was assumed that $R = q$ ($q = e^2/2\epsilon kT$ is the Bjerrum distance, where e is the elementary charge and k the Boltzmann constant). The assumption that $R = q$ has no practical effect on the standard EMF values determined. Table 1 contains the values of the standard EMF of the above-mentioned cell obtained at six temperatures.

The values of the free enthalpy of transfer from water to the systems under investigation was calculated from

$$\Delta G_t^{\ominus} = -F(E^{\ominus \text{mix}} - E^{\ominus \text{w}}) \tag{2}$$

where $E^{\ominus \text{mix}}$ is the standard EMF in mixed solvent and $E^{\ominus \text{w}}$ the standard EMF in water.

The values of $\Delta G_t^{\ominus}$ obtained by us and those of other authors for 298.15 K are given in Table 2.

TABLE 2

Values of $\Delta G_t^{\ominus}$ (J mol^{-1}) cited in the literature and obtained in the present study

THF (mol%)	Literature data [a]		Our results
	Ref. 7 [b]	Ref. 25 [c]	
1.0	689	843	646
2.5	1672	2027	1631
5.0	3184	3809	3001
7.5	4556	5389	4014
10.0	5807	6799	5442
15.0	8046	9288	7884
20.0	10129	11594	9795
25.0	12320	14033	11946
30.0	14928	16928	13954

[a] Interpolated values.

[b] Results obtained by means of glass sodium electrode.

[c] Results obtained by the vapour pressure measurement.

From eqn. (2) and the definition of entropy of transfer, the following relationship results:

$$\Delta S_t^{\ominus} = -\frac{\partial\, \Delta G_t^{\ominus}}{\partial T} = F\left(\frac{\partial E^{\ominus \mathrm{mix}}}{\partial T}\right) - F\left(\frac{\partial E^{\ominus \mathrm{w}}}{\partial T}\right) \tag{3}$$

The dependence $E^{\ominus} = f(T)$ was approximated with the polynomial

$$E^{\ominus} = a + bT + cT^2 \tag{4}$$

Hence

$$\left(\frac{\partial E^{\ominus}}{\partial T}\right)_p = b + 2cT \tag{5}$$

The values of $\Delta S_t^{\ominus}$ obtained from eqns. (3) and (5) allowed the enthalpy of transfer to be calculated:

$$\Delta H_t^{\ominus} = \Delta G_t^{\ominus} + T\Delta S_t^{\ominus} \tag{6}$$

The values of the coefficients a, b and c of the polynomial (4) and those of $\partial E_t^{\ominus}/\partial T$ obtained from eqn. (5) are given in Table 3.

Table 4 contains the values of the function $-T\Delta S_t^{\ominus}$ calculated from $\Delta G_t^{\ominus}$ and $\Delta H_t^{\ominus}$ values given in the literature and from our own results.

The values of $\Delta H_t^{\ominus}$ both from the literature and from the present study are given in Table 5.

The functions $\Delta G_t^{\ominus} = f(x)$, $-T\Delta S_t^{\ominus} = f(x)$ and $\Delta H_t^{\ominus} = f(x)$ (where x is in wt.%) obtained in the present work and those from the literature are illustrated in Figs. 1–3.

As seen from Fig. 1, the functions $\Delta G_t^{\ominus} = f(x)$ are almost linear and their shapes do not depend on the measurement method. At 5 mol% THF our

TABLE 3

Values of the coefficients a, b and c of the polynomial (4) and values of $(\partial E^{\ominus}/\partial T)_p$ from eqn. (5) at 298.15 K

THF (mol%)	a	$b \times 10^3$	$c \times 10^6$	$(\partial E^{\ominus}/\partial T)_p \times 10^3$
0	−0.1490	0.5213	−1.4735	−0.3573
1.0	−0.08748	0.07058	−7.2867	−0.3639
2.5	−0.1552	0.4633	−1.3991	−0.3710
5.0	−0.2248	0.8479	−2.057	−0.3839
7.5	−0.1662	0.3956	−1.358	−0.3950
10.0	−0.1842	0.4296	−1.4020	−0.4064
15.0	−0.3578	1.4560	−3.1783	−0.4392
20.0	−0.09064	−0.4366	−0.05888	−0.4717
25.0	−0.04106	−0.8786	−0.6147	−0.5121
30.0	−0.06122	−1.6011	1.6573	−0.6129

TABLE 4

Values of $-T\Delta S_t^{\ominus}$ (J mol^{-1}) calculated from values of $\Delta G_t^{\ominus}$ and $\Delta H_t^{\ominus}$ cited in the literature and obtained in the present study

THF (mol%)	Literature data		Our results
	Refs. 7, 20, 26	Refs. 20, 25, 26	
1.0	259	413	191
2.5	562	917	394
5.0	1070	1695	765
7.5	1395	2228	1085
10.0	2395	3387	1413
15.0	3145	4387	2355
20.0	4240	5705	3289
25.0	5841	7554	4454
30.0	8621	10621	7352

TABLE 5

Values of $\Delta H_t^{\ominus}$(NaCl) (J mol^{-1}) cited in the literature and obtained in the present study

THF (mol%)	Literature data		Our results
	Refs. 20, 26 [a]	Ref. 27 [a,b]	
1.0	430 [b]	1000	456
2.5	1110	1350	1238
5.0	2114	2040	2236
7.5	3161		2929
10.0	3412		4029
15.0	4901		5529
20.0	5889		6478
25.0	6479		7492
30.0	6307		6602
35.0	5642		

[a] Values obtained from calorimetric investigation.

[b] Interpolated values.

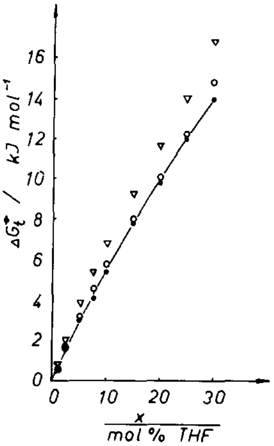

Fig. 1. The free enthalpy of transfer $\Delta G_t^\ominus$ of NaCl in water–THF mixtures at 298.15 K: ●, our results; ○, ref. 7; ▿, ref. 25.

results are different by at most 200 J mol^{-1} from those of Juillard et al. [7] obtained with cells containing a glass electrode and 600 J mol^{-1} from the results of Treiner [25] obtained by the vapour pressure method.

Kundu and co-workers [14,15], on the basis of their own results obtained by measuring the EMF of cells with an amalgam electrode, assert that the values of $\Delta G_t^\ominus$ obtained with glass electrodes in mixed solvents consisting of water–aprotic cosolvent are too high (see also ref. 4). Hence they have concluded that glass electrodes are not suitable for measuring $\Delta G_t^\ominus$ in water–aprotic solvents mixtures. Such an opinion seems to be too inflexible to us as we have already suggested [4]. The curve $\Delta G_t^\ominus = f(x)$ in the studies of all the above-mentioned authors exhibits an inconsiderable change in

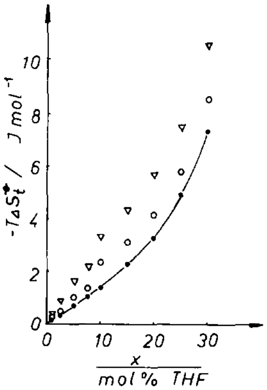

Fig. 2. Values of $-T\Delta S_t^\ominus$ of NaCl in water–THF mixtures at 298.15 K: ●, our results; ○, values calculated from data contained in refs. 7, 20 and 26; ▿, values calculated from data contained in refs. 20, 25 and 26.

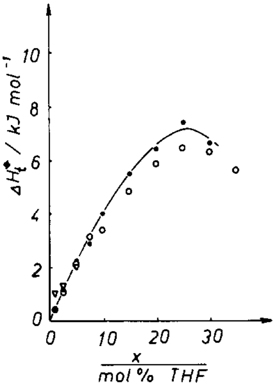

Fig. 3. The enthalpy of transfer $\Delta H_t^{\ominus}$ of NaCl at 298.15 K: ●, our results; ○, refs. 20 and 26; ▽, ref. 27.

slope starting from a THF content of about 10–15 mol%, which, at the low permittivity of THF ($\epsilon = 7.3$ [22]), could be due to the fact that the ionic association is not taken into account in those studies.

Figure 2 illustrates the function $-T\Delta S_t^{\ominus} = f(x)$ and includes also data from the literature. As seen, this function grows monotonically with increasing THF content.

The comparison of this function with the values calculated from thermochemical [20,26] and electrochemical [7] data and from the vapour pressure results [25] shows that the differences between values obtained from different data increase with increasing THF content. Maximum discrepancies are about 2 kJ K^{-1}. In addition, the scatter of our experimental results is lower than the other results.

It is characteristic that such substantial differences are not observed in the values of $\Delta H_t^{\ominus}$. The function $\Delta H_t^{\ominus} = f(x)$ (Fig. 3) exhibits a characteristic maximum in the case of the mixture containing 25 mol% THF independently of the measurement method used. The largest differences between the results of the present authors and those cited from the literature [20,26] are here lower than those in the case of $\Delta G_t^{\ominus}$, i.e. about 1 kJ mol^{-1}.

Considering that the literature data are concerned with direct calorimetric measurement, the results obtained in this study seem to be quite satisfactory.

The authors are inclined to think that the values of the entropy of transfer are consequently also better than those cited previously from the literature.

This points to analogous possibilities, as in case of water–alcohol systems [1–3], of effective determination of the enthalpy of transfer by electrochemical methods from temperature coefficients of the standard EMF.

The authors are also aware that it is necessary to carry out further studies on ionic association in solvents with relatively low electric permittivities. If the ionic association is not taken into account, additional errors in determining the values of the thermodynamic functions may quite possibly occur.

The reported results of studies on solutions of NaCl, NaBr and NaI in the water–DMF system at a single temperature [4] and the results of the present study concerning NaCl in water–THF system within a wide temperature range confirm, in the authors' opinion, the applicability of the glass electrode for thermodynamic investigations also in mixed solvents consisting of water and an aprotic solvent. Admittedly the studies were limited to 30 mol% THF, but the scope of examination in the water–DMF system was extended to pure DMF [4].

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