Adam Bald*, Jerzy Gregorowicz*

APPLICATION OF THE CELL: GLASS ELECTRODE (Na)|NaBr|AgBr, Ag
FOR THERMODYNAMIC STUDIES OF NaBr SOLUTIONS
IN WATER-ISOPROPYL ALCOHOL MIXTURES

Values of electromotive force (EMF) of the cell: glass electrode (Na)|NaBr|AgBr, Ag in water-isopropanol mixtures containing 0, 10, 30 and 50 wt % alcohol have been measured at 293.15, 303.15 and 313.15 K. Values of the standard EMF and thermodynamic functions of transfer of NaBr (ΔG^0, ΔS^0, ΔH^0) have been determined. The mean activity coefficients were also calculated.

This work is a continuation of our earlier researches [1-6] concerning the applications of the glass electrodes reversible towards cations for thermodynamic investigations of electrolyte solutions in mixed solvents. The review of the opinions of other authors was made in paper [1]. In our earlier papers [2-6] values of the free enthalpies, enthalpies and entropies of transfer of electrolytes were calculated from EMF data of the cells with the ionselective electrodes. They were compared with the results obtained from EMF measurements of the cells with the amalgam electrode, vapour pressure measurements and calorimetric measurements. In our opinion such procedure is the best way of verification of the obtained results. It was also shown from our earlier research that the comparison of the values of the enthalpies of transfer of electrolytes calculated from the temperature coefficients of EMF and calorimetric investigations lead us to the conclusion that the glass ion-selective electrodes are characterized

* Institute of Chemistry, University of Łódź, Poland.

by excellent accuracy, reproducibility   and the simplicity of   the
method of taking measurements. The aim   of our present paper is   to
compare the results reported here   with those   obtained in   studies
with the use the amalgam electrode [7].

EXPERIMENTAL

Reagents

NaBr P.O.Ch. - Gliwice, p.a.   was cristallized twice from redi-
stilled water and dried under reduced pressure   at   about 335 K.
Isopropyl alcohol P.O.Ch. - Gliwice, p.a.   was dried over molecular
sieves 4 A and distilled twice. Water   was distilled twice   from   a
basic $KMnO_4$ solution.

Apparatus and procedure

Sodium glass electrodes reversible   towards   sodium   ions type
ESL-51G-05 (made USSR) and silver-silver chloride electrodes produ-
ced by the thermal-electrolytic method [8]   were   used. Only   those
silver-silver chloride electrodes were used whose potentials varied
not more than by 0.05 mV.

The measuring cell was made of Pyrex glass closed tight with   a
teflon cover with a teflon stirrer. The cell   was   surrounded   by a
steel shield and placed in a thermostat of our design. Paraffin oil
was used as a thermostating liquid. Stability of   temperature was
better than 0.01 K. Electromotive forces was measured by means of a
precise pH-meter type OP-208/1 (made by Radelkis). connected with a
printer. To provide a high accuracy the solutions were prepared   by
the weight method by adding subsquent amount   of   stock   solution.
Detailed description of the measuring method is contained in   paper
[2, 3].

*   Institute of Chemistry, University of Łódź, Poland.

RESULTS AND DISCUSSION

Table 1 contains values of EMF of the cell: glass electrode (Na)|NaBr|AgBr, Ag at 293.15, 303.15 and 313.15 K for various electrolyte concentrations in water-isopropanol mixtures containing: 0, 10, 30 and 50 wt % of alcohol.

T a b l e   1

EMF values of the investigated cells

m	E_{293}	E_{303}	E_{313}	m	E_{293}	E_{303}	E_{313}
	0 wt. % i-PrOH				10 wt. % i-PrOH		
0.01560	-0.0568	-0.0510	-0.0457	0.01243	-0.0661	-0.0596	-0.0537
0.02437	-0.0779	-0.0730	-0.0687	0.01876	-0.0858	-0.0798	-0.0547
0.03683	-0.0976	-0.0931	-0.0895	0.02775	-0.1044	-0.0989	-0.0941
0.04339	-0.1052	-0.1010	-0.0977	0.03807	-0.1192	-0.1142	-0.1098
0.05180	-0.1137	-0.1096	-0.1067	0.04798	-0.1302	-0.1255	-0.1213
0.06686	-0.1256	-0.1220	-0.1194	0.05830	-0.1395	-0.1348	-0.1309
0.07223	-0.1293	-0.1257	-0.1232	0.06641	-0.1453	-0.1410	-0.1373
				0.07221	-0.1494	-0.1450	-0.1414
	30 wt. % i-PrOH				50 wt. % i-PrOH		
0.00916	-0.0867	-0.0808	-0.0755	0.01341	-0.1428	-0.1386	-0.1346
0.01683	-0.1151	-0.1100	-0.1054	0.01358	-0.1431	-0.1388	-0.1352
0.02634	-0.1357	-0.1310	-0.1271	0.01440	-0.1459	-0.1415	-0.1378
0.03579	-0.1500	-0.1459	-0.1424	0.02668	-0.1736	-0.1695	-0.1663
0.04295	-0.1581	-0.1542	-0.1507	0.03257	-0.1823	-0.1790	-0.1761
0.05005	-0.1650	-0.1610	-0.1579	0.03788	-0.1890	-0.1853	-0.1825
0.05868	-0.1722	-0.1687	-0.1658	0.03875	-0.1895	-0.1862	-0.1841
				0.04078	-0.1916	-0.1881	-0.1860
				0.04463	-0.1961	-0.1927	-0.1901
				0.04635	-0.1973	-0.1937	-0.1919
				0.05333	-0.2033	-0.2010	-0.1983
				0.06014	-0.2087	-0.2053	-0.2034
				0.06682	-0.2131	-0.2099	-0.2083
				0.06975	-0.2153	-0.2121	-0.2102
				0.09073	-0.2264	-0.2237	-0.2222
				0.11110	-0.2353	-0.2325	-0.2313

The values of standard EMF of the investigated cell were determined by linear extrapolation of function (1) up to concentration m = 0

$$f(m) = E + \frac{2R_g T}{F} \ln m - \frac{2R_g T}{F} \frac{Ad_o^{0.5} m^{0.5}}{1 + BR d_o^{0.5} m^{0.5}} - \frac{2R_g T}{F} \ln(1 + 0.002 \, mM) =$$

$$= E^o - \frac{2R_g T}{F} Cm \tag{1}$$

where:

$A = (\ln 10) 1.8246 \cdot 10^6 / (\varepsilon T)^{1.5}$,

$B = 50.29 / (\varepsilon T)^{0.5}$,

R_g - gas constant $[J \cdot mole^{-1} K^{-1}]$,

T - temperature $[K]$,

d_o - solvent density $[kg \cdot dm^{-1}]$,

ε - electric permittivity of solvent,

R - distance parameter of ions $[\mathring{A}]$,

F - the Faraday constant $[C \cdot mol^{-1}]$,

m - molality $[mole \cdot kg^{-1}]$,

M - solvent molecular mass.

Function (1) is obtained by inserting H u c k e l's equation [9] expressed in the molal scale

$$\ln \gamma_\pm = - \frac{Ad_o^{0.5} m^{0.5}}{1 + BR d_o^{0.5} m^{0.5}} + Cm - \ln(1 + 0.002 \, mM) \tag{2}$$

to the following equation describing the EMF of the cell studied

$$E = E^o - \frac{2R_g T}{F} \ln m \tag{3}$$

where: $\gamma_\pm$ - mean activity coefficient in molal scale.

Parameter R was assumed according to the often applied   J u s t i c e   proposition [10, 11] as equal to the   B j e r r u m critical distance q [12]:

$$q = \frac{|z_+ z_-| e^2}{2\varepsilon kT} \tag{4}$$

where:

e - elementary charge,

z_+, z_- - cation and anion charge number respectively,

k - Boltzmann's constant.

In order to be able to compare the obtained results with ones given in literature [7] calculations were made also for $R = 4$ Å. The desity (d_0) and electric permittivity (ε) necessary for calculations were obtained by interpolation of data presented in papers [13, 14]. The obtained values of E^0 for $R = q$ and $R = 4$ Å are collected in Tab. 2. As can be seen from Tab. 2 values of E^0 for $R = q$ and $R = 4$ Å are not significantly different for mixtures

T a b l e   2

Standard EMF values of cell: glass electrode (Na)|NaBr|AgBr, Ag

wt. % i-PrOH	E_m^0/ V					
	293.15 K		303.15 K		313.15 K	
	$R = q$	$R = 4$ Å	$R = q$	$R = 4$ Å	$R = q$	$R = 4$ Å
0	-0.2731 ±0.0001 q = 3.55 Å	-0.2730 ±0.0001	0.2749 ±0.0001 q = 3.59 Å	-0.2749 ±0.0001	-0.2772 ±0.0001 q = 3.64 Å	-0.2772 ±0.0001
10	-0.2941 ±0.0001 q = 3.90 Å	-0.2941 ±0.0001	-0.2956 ±0.0001 q = 3.95 Å	-0.2956 ±0.0001	-0.2977 ±0.0001 q = 4.02 Å	-0.2977 ±0.0001
30	-0.3313 ±0.0001 q = 4.88 Å	-0.3314 ±0.0001	-0.3339 ±0.0002 q = 4.98 Å	-0.3340 ±0.0002	-0.3371 ±0.0002 q = 5.06 Å	-0.3372 ±0.0002
50	-0.3758 ±0.0002 q = 7.85 Å	-0.3778 ±0.0004	-0.3796 ±0.0003 q = 8.02 Å	-0.3819 ±0.0004	-0.3842 ±0.0003 q = 8.22 Å	-0.3867 ±0.0003

containing 0, 10 and 30 wt % isopropyl alcohol. The differences are within the limits of standard error of the values of standard EMF data. The more significant differences ca. 2-2.5 mV are observed for the mixture containing 50 wt % alcohol. This is connected with the fact, that the q parameter is ca. twice higher than 4 Å. The lower standard error of E^0 indicates that the assumption $R = q$ appears to be correct for mixtures with higher alcohol content.

The values of free enthalpy of transfer of NaBr ΔG_t^O were calculated on the basis of the following relationship

$$\Delta G_t^O = F(E^{Om} - E^{OW}) \tag{5}$$

where:

E^{Om} - standard EMF of the cell in the mixed solvent,

E^{OW} - standard EMF of the cell in water.

The relation $\Delta G_t^O = f(T)$ was approximated by the polynominal $\Delta G_t^O = a + bT$. The entropy of transfer was calculated applying the equation

$$\Delta S_t^O = -\left(\frac{\partial \Delta G_t^O}{\partial T}\right)_p \tag{6}$$

The ΔS_t^O values calculated on the basis of eq. (6) were used for calculating the enthalpy of transfer

$$\Delta H_t^O = \Delta G_t^O + T \Delta S_t^O \tag{7}$$

The values of the thermodynamic functions calculated as mantioned above are in molality scale. M e k j a v i ć [7] presented the values of the thermodynamic functions in mole fraction scale with the assumption R = 4. That is the reason for giving the thermodynamic functions expressed on mole fraction scale apart from ones on molality scale with the assumption R = q. They are collected in Tab. 3. The calculation were made using the following expressions

$$\Delta G_{tx}^O = \Delta G_{tm}^O - 2R_g T \ln \frac{M_s}{M_w} \tag{8a}$$

$$\Delta S_{tx}^O = -\left(\frac{\partial \Delta G_{tx}^O}{\partial T}\right)_p = \Delta S_{tm}^O + 2R_g \ln \frac{M_s}{M_w} \tag{8b}$$

$$\Delta H_{tx}^O = \Delta H_{tm}^O = \Delta G_{tx}^O + T \Delta S_{tx}^O \tag{8c}$$

where:

M_s - molecular mass of mixed solvent,

M_w - molecular mass of water,
x - index for mole fraction scale,
m - index for molality scale.

Table 3

Values of thermodynamic functions of transfer of NaBr
from water to the mixed solvent

wt. % i-PrOH	scale	R	ΔG_t^o/J·mol^{-1}			ΔS_t^o J·mol^{-1}K^{-1}	ΔH_t^o J·mol^{-1}
			293.15 K	303.15 K	313.15 K	303.15 K	303.15 K
10	m	q	2 027	1 997	1 978	2.5	2 758
	x	q	1 679	1 637	1 605	3.7	2 758
	x*	4 A	1 800	1 820	1 660	7.2	4 000
30	m	q	5 617	5 693	5 781	-8.2	3 208
	x	q	4 473	4 510	4 559	-4.3	3 208
	x*	4 A	4 480	4 590	4 570	-4.3	3 290
50	m	q	9 900	10 104	10 326	-21.3	3 650
	x	q	7 805	7 938	8 089	-14.2	3 650
	x	4 A	8 018	8 160	8 330	-15.6	3 453
	x*	4 A	8 200	8 390	8 540	-16.9	3 270

* Values from paper [7].

For mixtures containing 10 and 30 wt % alcohol the thermodynamic functions ΔG_{tx}^o, ΔS_{tx}^o and ΔH_{tx}^o were obtained only on the basis of the assumption R = q. In these mixtures the values of the functions mentioned above for both R = q and R = 4 Å   assumptions should be identical within limits of experimental error because the standard EMF values are almost the same. For the mixtures containing 50 wt % isopropyl alcohol the values of ΔG_{tx}^o, ΔH_{tx}^o,   and ΔS_{tx}^o were calculated using both assumption R = q, R = 4 Å. Such a procedure made it possible to make a more detailed comparison of the results obtained from EMF of the cell with sodium glass electrodes with M e k j a v i ć   et al. data [7] based on studies using the amalgam electrodes. Some M e k j a v i ć's   data are also included in Tab. 3.

Analysis of the results collected in Tab. 3 leads us to following conclusions:

a) The maximum difference between our results of ΔG_{tx}^{0} and those reported by M e k j a v i ć [7] are ca. 200 J, which corresponds to a change of ca. 2 mV for electromotive force values.

b) The temperatur changes of our ΔG_{tx}^{0} values are more regular in comparison with M e k j a v i ć's results. In the mixtures containing 10 wt % alcohol our values of ΔG_{tx}^{0} slightly decrease with the increase in temperature. M e k j a v i ć's results [7] show a slight increase in the temperature range 293-303 K while a considerable decrease is observed in the temperature range 303-313 K. For mixtures with 30 wt % of isopropyl alcohol our values of ΔG_{tx}^{0} slightly increase together with the increase of temperature while the dependence $\Delta G_{tx}^{0} = f(T)$ found by M e k j a v i ć shows extreme. Only for mixtures with 50 wt % alcohol our and M e k j a v i ć's dependences of ΔG_{tx}^{0} vs. temperature exhibit similar behaviour.

c) The differences in the behaviour of the functions $\Delta G_{tx}^{0} = f(T)$ affect the analogous dependences for ΔS_{tx}^{0} and ΔH_{tx}^{0}. They are most pronounced for the mixture containing 10 wt % alcohol.

In our opinion M e k j a v i ć's et al. results of ΔH_{tx}^{0} and S_{tx}^{0} at 293 and 313 K are not reliable because the determination of the derivatives from the dependence $\Delta G_{tx}^{0} = f(T)$ based on just three points cannot possibly be very accurate. The M e k j a v i ć's et al. ΔG_{tx}^{0} values (Tab. 3) suggest that the values of ΔS_{tx}^{0} and ΔH_{tx}^{0} increase with temperature and even they change their sign for the mixtures cintaining 10 and 30 wt % alcohol. Analysing our data of ΔG_{tx}^{0} shown in Tab. 3 we can notice the decreasing of the enthalpy and entropy of transfer of electrolyte with the increase in temperature. The same results were obtained from the measurements of enthalpy of solution of alkali metal halides [15, 16]. The differences between the results found from more direct method of measurements of enthalpy of solution of electrolyte and obtained by M e k j a v i ć's et al. [7] for amalgam electrodes may be connected with their incorrect values of the temperature coefficients of the standard EMF. Values of the temperature coefficients of the standard EMF depend on the values of standard EMF. It is evident from equation (1) that an error of the standard EMF values may be connected with an error of C coefficient. The value of the C

coefficients according to equation (2) affects the values of the activity coefficient of electrolyte.

T a b l e   4

Activity coefficients $\gamma_\pm$ of natrium bromide

wt. % i-PrOH	T K	R	m/mol·kg^{-1}					
			0.01	0.02	0.05	0.10	0.15	0.20
10	293	q	0.892	0.860	0.810	0.771	0.752	0.741
		4 A*	0.893	0.861	0.812	0.774	0.755	0.745
	303	q	0.889	0.855	0.800	0.755	0.730	0.713
		4 A*	0.890	0.856	0.802	0.760	0.736	0.722
	313	q	0.886	0.850	0.791	0.740	0.709	0.687
		4 A*	0.888	0.854	0.801	0.759	0.736	0.722
30	293	q	0.856	0.812	0.744	0.685	0.649	0.623
		4 A*	0.858	0.818	0.758	0.717	0.699	0.691
	303	q	0.851	0.806	0.732	0.669	0.627	0.597
		4 A*	0.853	0.811	0.746	0.699	0.675	0.661
	313	q	0.848	0.801	0.724	0.656	0.611	0.577
		4 A*	0.849	0.805	0.737	0.685	0.657	0.639
50	293	q	0.763	0.706	0.626	0.565	0.528	0.502
		4 A	0.744	0.681	0.598	0.547	0.530	0.526
		4 A*	0.740	0.672	0.580	0.515	0.483	0.465
	303	q	0.757	0.698	0.614	0.545	0.502	0.470
		4 A	0.737	0.671	0.583	0.526	0.503	0.494
		4 A*	0.735	0.669	0.578	0.517	0.490	0.476
	313	q	0.751	0.692	0.606	0.536	0.492	0.458
		4 A	0.730	0.663	0.573	0.517	0.493	0.487
		4 A*	0.728	0.661	0.570	0.510	0.484	0.471

* Values calculated from EMF data contained in paper [7].

It was a reason why we decided to compare our values of electrolyte activity coefficients with those obtained by M e k j a v i ć et al. [7] (Tab. 4). For the mixture   containing 50 wt % isopropyl alcohol our q value is distinctly different   from 4 Å i.e. the value used for calculation by M e k j a v i ć   et al.   Thus   the activity coefficients, $\gamma_\pm$ from our EMF data were also calculated

for assumption R = 4 Å. The results were collected in Tab. 4. Our
mean activity coefficients decrease together with the increase of
temperature for each molality of the solution.

Taking into consideration the equation

$$\frac{\partial \ln \gamma_\pm}{\partial T} = -\frac{\bar{L}_2}{2RT^2} \tag{9}$$

we may notice that the relative partial molar enthalpies of electro-
lyte, $\bar{L}_2$, are positive for all salt concentrations and for all
investigated temperatures. The dependences $\gamma_\pm = f(T)$ found by
M e k j a v i ć et al. show extrema in solution with higher
molality for 50 wt % isopropyl alcohol or the $\gamma_\pm$ values irregularly
decrease with the increase in temperature.

In conclusion it may be noted that the values of the free
enthalpy of transfer determined in this study on the basis of the
EMF data of the cells with glass electrodes and those ones using
the amalgam electrodes are not distinctly different. The application
the ΔG_t^0 values mentioned above and the enthalpy of transfer
values obtained from measurements of enthalpy of solution of elec-
trolyte to calculation the entropy of transfer ($\Delta S_t^0 = (\Delta H_t^0 - \Delta G_t^0)/T$)
show that the obtained ΔS_t^0 values are not significantly different.
On the other hand if the EMF data were used in order to determine
the entropy and enthalpy of transfer then in our opinion the appli-
cation of the EMF data of the cells with glass electrodes lead to
more reliable results.

REFERENCES

[1] Z. K o z ł o w s k i, A. B a l d, J. G r e g o r o w i c z,
    A. S z e j g i s, Acta Univ. Lodz., Folia Chim., 7, 11 (1987).
[2] Z. K o z ł o w s k i, A. B a l d, J. G r e g o r o w i c z,
    A. S z e j g i s, Acta Univ. Lodz., Folia Chim., 7, 4 (1987).
[3] Z. K o z ł o w s k i, A. B a l d, J. G r e g o r o w i c z,
    A. S z e j g i s, Pol. J. Chem., 61, 475 (1987).

[4] Z. K o z ł o w s k i, A. B a l d, J. G r e g o r o w i c z,
A. S z e j g·i s, Pol. J. Chem., 64, 167 (1990).

[5] Z. K o z ł o w s k i, A. B a l d, J. G r e g o r o w i c z,
A. S z e j g i s, Thermochim. Acta, 170, 217 (1990).

[6] J. G r e g o r o w i c z, Doctoral thesis, University of
Łódź 1990.

[7] J. R a d o š e v i ć, I. M e k j a v i ć, Electrochim. Acta,
28, 1435 (1983).

[8] B. J. I v e s, G. J. J a n z, References Electrodes, New
York 1961.

[9] E. H u c k e l, Phys. Z., 26, 93 (1925).

[10] J. C. J u s t i c e, J. Chim. Phys., 65, 353 (1968).

[11] J. C. J u s t i c e, Electrochim. Acta, 18, 701 (1971).

[12] N. B j e r r u m, Kgl. Danske Videnskab Selskab. Mat.-Fys.
Medd., 7, 230 (1926).

[13] G. A k e r l o f, J. Am. Chem. Soc., 54, 4125 (1923).

[14] R. L. M o o r e, W. A. F e l s i n g, J. Am. Chem. Soc.,
69, 1076 (1947).

[15] H. P i e k a r s k i, A. P i e k a r s k a, S. T a n i e-
w s k a-O s i ń s k a, Can. J. Chem., 62, 856 (1984).

[16] A. I. P i r o g o v, Doctoral Thesis, IChTI Ivanovo 1971.

Adam Bald, Jerzy Gregorowicz

ZASTOSOWANIE OGNIWA: SZKLANA ELEKTRODA (Na)|NaBr|AgBr, Ag
DO TERMODYNAMICZNYCH BADAŃ ROZTWORÓW NaBr
W MIESZANINACH WODA-ALKOHOL IZOPROPYLOWY

    Zmierzono wartości sił elektromotorycznych   ogniwa: elektroda
szklana (Na)|NaBr|AgBr, Ag w mieszaninach wody z izopropanolem o
zawartości 0, 10, 30 i 50 % wag. alkoholu w temperaturach 293,15,
303,15 i 313,15 K. Wyznaczono wartości SEM standardowych ogniwa i
termodynamicznych funkcji przeniesienia NaBr z wody do badanych
mieszanin (ΔG$_t^0$, ΔS$_t^0$,   ΔH$_t^0$). Ponadto wyznaczono wartości średnich
współczynników aktywności elektrolitu. Uzyskane wartości porównano
z analogicznymi danymi otrzymanymi przez innych autorów metodą po-
miaru sił elektromotorycznych ogniw zawierających elektrodę amalga-
matową.