A C T A U N I V E R S I T A T I S L O D Z I E N S I S
FOLIA CHIMICA 7, 1987

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FREE ENTHALPY OF TRANSFER OF NaI FROM WATER TO WATER-METHANOL MIXTURES AT THE TEMPERATURE OF 298.15 K

EMF values of the cell: glass el. Na | NaI | AgI, Ag were measured in methanol-water mixtures at the temperature of 298.15 K within the full composition range of the mixed solvent. Values of standard EMF and of free enthalpy of transfer of NaI from water to the mixed solvent were determined. The obtained values of ΔG_t^o were compared with those obtained by other authores by EMF measurements of amalgam electrode cell.

In recent years many authors have determined the free enthalpy of transfer of electrolyte by the method of measuring EMF of cells containing glass electrodes reversible to monovalent metal cations in water-organic solvent mixtures. The accuracy of this method and its theoretical principles are subject of intensive studies which have been reviewed by the authors of the present paper [1].

The methanol-water system is one of mixed solvents which have been quite thoroughly examined. Values of free enthalpy of the NaI transfer from water into these mixtures are available in the literature [2-4]. The object of the present study was dictated by the possibility to compare the ΔG_t^o values from the literature with corresponding values obtained by the authors.

EXPERIMENTAL

Reagents

NaI (POCh-Gliwice, analar grade) was crystalized twice from redistilled water and dried under vacuum at about 335 K.

Methyl alcohol (POCh-Gliwice, analar grade) was dried on 4A molecular sieves and distilled twice.

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

Apparatus

The EMF of cells was measured with a OP-208/1 pH-meter (Radelkis) including a OH 814/1 recorder (Radelkis) and a ERD-103 (printer Zootechnika - Cracow) coupled with a digital time-recorder. The measurement cell consisted of a Pyrex glass vessel with a tight teflon cover in which a teflon stirrer and electrodes were mounted.

Measurements were carried out with a ESL-51G-05 glass electrode (made in USSR), reversible to sodium ions and a silver - silver iodide electrode prepared by the thermal-electrolytic method [5]. Only electrodes with potential differences lower than 0.05 mV were used.

The whole cell was enclosed with a steel screen and placed in a thermostat containing paraffin oil. The part of the screen immersed in the oil was made of a net to provide good heat exchange between the cell and the thermostating liquid.

Temperature was controlled with a thermistor in a system of Wheatstone bridge with an accuracy of 0.01 K.

Measurement method

All the operations associated with the preparation of solutions were carried out by the gravimetric method. First, the mixed solvent of required composition was prepared. A known amount of that solvent was placed in the cell. To some part of the solvent precisely weighed of NaI was added to obtain a stock solution. Known quantities of that NaI solution were introduced into the cell vessel obtaining a solution of known concentration. Previously in the measurement vessel were placed: the silver-silver iodide electrode thoroughly washed with the solvent under investigation und the glass electrode stored for 1-2 days in the solvent of the same composition. Values of EMF of the cell were read and recorded at constant temperature 298.15 K. The value which

was constant for sufficiently long period of time (about 1 hour) was accepted as the proper one. Next, a new portion of the stock NaI solution was added to the measurement vessel and the next EMF value was measured.

RESULTS AND DISCUSSION

Table 1 contains values of the EMF of the cell: glass el. Na|NaI|AgI, Ag at the temperature of 298.15 K for various electrolyte concentrations in water-methanol mixtures containing 0.00, 5.78, 10.55, 22.84, 30.87, 51.43, 75.93, 93.73 and 100.00 mol per cent of methanol, respectively. There are quoted also densities and electric permittivities of solvent which were obtained by the interpolation of data from papers [6, 7].

The E^{o} values of the electromotive force of the investigated cell were determined by the method of H i t c h c o c k [8] through the extrapolation of the following function to zero concentration:

$$f(m) = E + \frac{2RT}{F} \ln m - \frac{2RT}{F} \cdot A \cdot d_o^{1/2} m^{1/2}$$

where:

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

d_o = solvent density,
ε = electric permittivity of the solvent.

Next, the values of the free enthalpy of transfer of NaI from water to subsequent mixtures were calculated:

$$\Delta G_t^o = - F(E^{om} - E^{ow})$$

where:

E^{om} - standard EMF in mixed solvent,
E^{ow} - standard EMF in water.

The values of standard EMF of the cell and the free enthalpy of electrolyte transfer are given in Tab. 2.

The Figure shows the function $\Delta G_t^o = f(x)$ obtained in the present study and values of ΔG_t^o obtained by other authors [2-4].

Table 1

EMF values of the investigated cells

0.00	$m \cdot 10^2$	1.015	1.5023	2.442	3.521	4.438	5.269	6.102	7.021	d_o	ε
% mol MeOH	E	-0.2550	-0.2744	-0.2981	-0.3161	-0.3275	-0.3360	-0.3523	-0.3502	0.9970	78.64
5.78	$m \cdot 10^2$	1.396	1.961	2.751	3.647	4.541	5.303	6.192	7.179	0.9800	74.1
% mol MeOH	E	-0.2850	-0.3009	-0.3166	-0.3302	-0.3407	-0.3480	-0.3554	-0.3625		
10.57	$m \cdot 10^2$	1.225	2.019	2.850	3.682	4.542	5.472	6.130	6.582	0.9684	70.3
% mol MeOH	E	-0.2860	-0.3104	-0.3268	-0.3394	-0.3494	-0.3585	-0.3639	-0.3676		
22.81	$m \cdot 10^2$	1.175	1.722	2.540	3.495	4.332	5.119	5.741	6.760	0.9420	62.0
% mol MeOH	E	-0.3015	-0.3196	-0.3382	-0.3531	-0.3629	-0.3710	-0.3761	-0.5441		
30.85	$m \cdot 10^2$	0.942	1.754	2.756	3.567	4.121	5.164	6.160	7.362	0.9232	57.4
% mol MeOH	E	-0.3020	-0.3320	-0.3539	-0.3660	-0.3729	-0.3842	-0.3925	-0.4011		
51.40	$m \cdot 10^2$	1.235	2.050	3.181	3.743	4.935	5.555	6.262	6.801	0.8786	47.0
% mol MeOH	E	-0.3441	-0.3678	-0.3877	-0.3952	-0.4079	-0.4131	-0.4189	-0.4225		
75.96	$m \cdot 10^2$	0.899	1.361	1.960	2.951	3.961	4.480	5.161	5.655	0.8300	37.8
% mol MeOH	E	-0.3636	-0.3823	-0.3990	-0.4168	-0.4305	-0.4357	-0.4418	-0.4466		
93.77	$m \cdot 10^2$	0.873	1.351	1.861	2.757	3.473	4.081	4.533	5.371	0.7972	33.0
% mol MeOH	E	-0.3820	-0.4011	-0.4156	-0.4325	-0.4423	-0.4498	-0.4542	-0.4616		
100.00	$m \cdot 10^2$	1.309	2.280	3.010	4.673	5.806	6.303	7.272	8.231	0.7866	31.5
% mol MeOH	E	-0.4056	-0.4292	-0.4414	-0.4598	-0.4695	-0.4736	-0.4794	-0.4848		

m - molality, E - EMF [V], ε - electric permittivity, d_o - solvent density [kg/dm^3]

Table 2

Standard EMF values of the investigation cell and the free enthalpy of NaI transfer ΔG_t^o

% mol MeOH	0.00	5.78	10.57	22.81	30.85	51.40	75.96	93.77	100.00
E^o [V]	-0.4960	-0.5102	-0.5185	-0.5377	-0.5491	-0.5813	-0.6193	-0.6412	-0.6485
ΔG_t^o [J/mol]	0	1370	2171	4024	5123	8230	11897	14010	14714

As can be seen from the Figure, the obtained values of ΔG_t^o show conformity with corresponding literature data. Our values of ΔG_t^o = = f(x) are contained within the range of analogous values obtained by other authors. It also follows from the analysis of the function ΔG_t^o = f(x) that:

a) the shape of ΔG_t^o = f(x) obtained by us is most similar to that obtained by F e a k i n s and coworkers [4],

b) at methanol content up to about 70-80% also the values of ΔG_t^o obtained by us show the best conformity with the data of Feakins.

It can be noticed that the differences between values of ΔG_t^o obtained by us with the glass electrode and those obtained by Feakins with the amalgam electrode are negligible at methanol content within the range from 0 to 30% mol (43% by wt.). These differences increase with increasing methanol content (about 500 j at about 90% ol, i.e. about 95% by wt. of MeOH). The highest differences takes place in pure methanol and reach about 1 kJ, which corresponds to a EMF difference of about 10 mV.

To sum up, it can be stated on the basis of the cited literature data that except of pure methanol the values of the free enthalpy of NaI transfer in water-methanol mixtures obtained in the present study are satisfactory. Such a conclusion supports the thesis that ionselctive glass electrodes can be used for thermodynamic use ionselective glass electrodes to study temperature relations of EMF, thus to determine entropy and enthalpy of transfer.

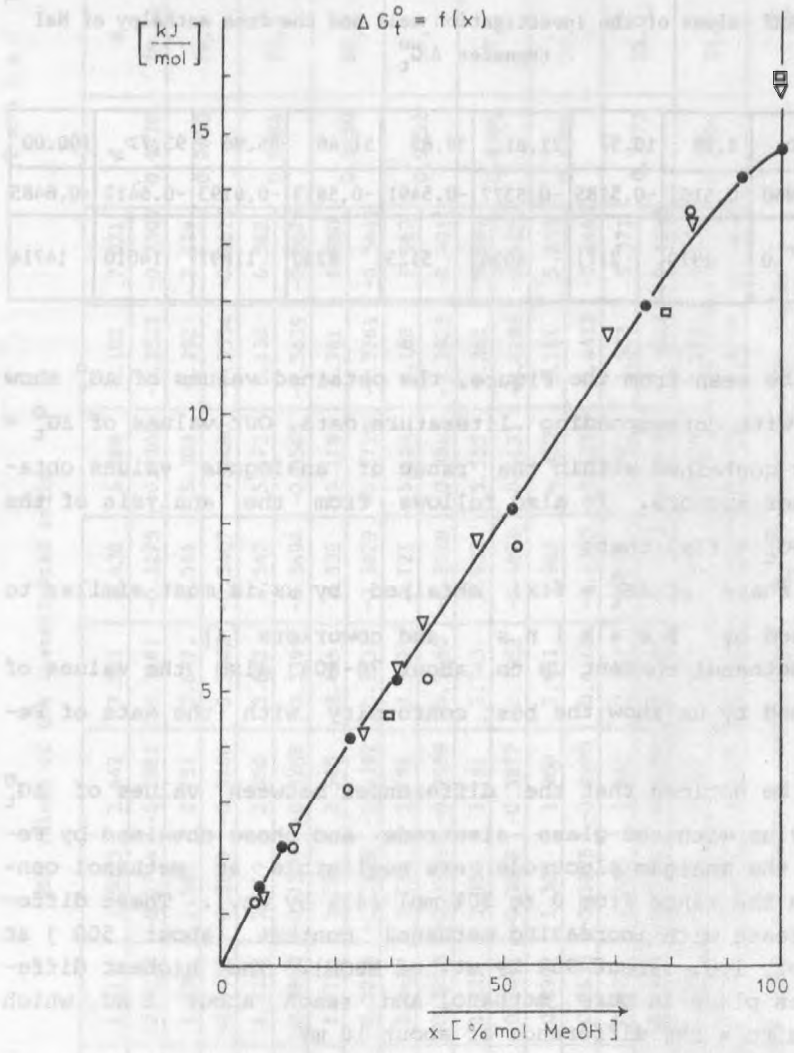

Fig. 1. The course of relation $\Delta G_t^o = f(x)$ of NaI in the mixtures H_2O-methanol: □ - ref. [2], o - ref. [3], ▽ - ref. [4], ● - own results

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SWOBODNA ENTALPIA PRZENIESIENIA NaI Z WODY
DO MIESZANIN WODA-METANOL W TEMPERATURZE 298,15 K

Zmierzono wartości SEM ogniwa el. szklana Na|NaI|AgI, Ag w mieszaninach metanol-woda w temperaturze 298,15 K w pełnym zakresie składu mieszanego rozpuszczalnika. Wyznaczono wartości SEM standardowej i wartości swobodnej entalpii przeniesienia NaI z wody do mieszanego rozpuszczalnika. Otrzymane wartości ΔG_t^o porównano z analogicznymi wartościami otrzymanymi przez innych autorów metodą pomiaru SEM ogniw z elektrodą amalgamatową. Z przeprowadzonych badań wynika możliwość stosowania szklanej elektrody sodowej do badań termodynamicznych własności roztworów elektrolitów.