STANDARD AND REVERSIBLE ANODIC POTENTIALS OF THE ELECTROSYNTHESIS OF PEROXODISULFATES AT 0–50 °C

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Standard potentials of the couples $S_2O_8^{2-}/SO_4^{2-}$ and $S_2O_8^{2-}/HSO_4^{-}$ in the temperature range 0–50 °C and reversible anodic potentials of the electrosynthesis of peroxodisulfates at various initial concentrations of M_2SO_4 and H_2SO_4, various conversion degree of sulfate to peroxodisulfate in the same temperature range under neglecting the effect of activity coefficients of reaction components have been derived. Reversible anodic potentials of the electrosynthesis of almost saturated solutions of ammonium peroxodisulfate in the temperature range 10–40 °C under various reaction conditions have been calculated on taking into account the corresponding activity coefficients. It has been shown that the reversible anodic potentials under respecting activity coefficients of reaction components are by about 20–30 mV higher. The results of this contribution can be applied to all chemical or electrochemical reactions of peroxodisulfates.

Keywords: Standard potential; Reversible potential; Electrosynthesis; Peroxodisulfates.

Peroxodisulfates are produced by the anodic oxidation of concentrated acidic solutions of corresponding sulfates on suitable anodes at high current densities and at low temperatures[1–3]. Until the sixties or seventies of the last century, they, mainly ammonium salt, served worldwide as the intermediate product of the industrial fabrication of hydrogen peroxide by several electrochemical methods[1,2]. Although these methods were later mostly substituted by more economical autoxidation methods[1–3], the industrial production of peroxodisulfates further continues due to their strong oxidizing, catalytic and promoting properties with applications in a series of branches[3]. Up to now, values of standard electrode potentials $E°(S_2O_8^{2-}/SO_4^{2-}) = 1.9389$ V and $E°(S_2O_8^{2-}/HSO_4^{-}) = 2.0569$ V at 25 °C were known[4]. These data were evaluated using the tabulated data of standard formation Gibbs energies, $\Delta_f G°$, of the corresponding substances[5]. Calculation of the standard anodic potentials of the electrosynthesis of peroxodisulfates at other temperatures was based on the results of the recent contribution[6]

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dealing with the estimation of sufficiently reliable values of standard thermodynamic data of peroxodisulfates at 0–50 °C. Rigorous calculation of the reversible anodic potentials of the given process at various reaction conditions is now possible using the recently derived values of mean activity coefficients of the reaction components in the appropriate almost saturated polycomponent solutions[7]. The results of this treatment are the subject of this contribution.

RESULTS AND DISCUSSION

The electrosynthesis of peroxodisulfates by anodic discharge of sulfate or hydrogen sulfate anion and cathodic discharge of hydrogen ion to gaseous hydrogen can be described by the following overall equations

$$2\ \mathrm{SO_4}^{2-} + 2\ \mathrm{H}^+ \pm 2\ \mathrm{e} = \mathrm{S_2O_8}^{2-} + \mathrm{H_2} \qquad (1)$$

and/or

$$2\ \mathrm{HSO_4}^{-} \pm 2\ \mathrm{e} = \mathrm{S_2O_8}^{2-} + \mathrm{H_2}\ . \qquad (2)$$

The temperature dependence of $\Delta_r G°$ (in J mol^{-1}) of both considered reactions in the range $t = 0–50$ °C (i.e. $T = 273.15–323.15$ K) can be described by the following expressions independent of the presence of other cations

$$\begin{aligned}\Delta_r G°_{(1)} = {} & 374160 - 334.328A - ((504.876 - 1.69337\ T)/B + (7821.19 - \\ & - 26.882T - 0.001783T^2 + 105000/T)/A)(A - BT)\end{aligned} \qquad (3)$$

and

$$\begin{aligned}\Delta_r G°_{(2)} = {} & 396920 - 110.884A - ((3.4668 - 0.01163T)/B + (7821.19 - \\ & - 26.882T - 0.001783T^2 + 105000/T)/A)(A - BT)\end{aligned} \qquad (4)$$

with $A = T - 298.15$ and $B = \ln (T/298.15)$. Consequently, for the temperature dependence of the standard potential difference $E°$ of the electrolytic cell with anodic production of peroxodisulfate ions and cathodic evolution of gaseous hydrogen by reaction (*1*) or (*2*), simultaneously denoting the standard anodic potentials of the electrosynthesis of peroxodisulfate ions, the following relations have been obtained

$$E^\circ_{(1)} = 1.93895 - 0.00173253A - ((0.00261634 - 8.77527 \times 10^{-6}T)/B + \\ + (0.04053 - 1.3931 \times 10^{-4}T - 9.23975 \times 10^{-9}T^2 + \\ + 0.544124/T)/A)(A - BT) \quad (5)$$

and

$$E^\circ_{(2)} = 2.05689 - 0.00057462A - ((1.7965 \times 10^{-5} - 6.0268 \times 10^{-8}\,T)/B + \\ + (0.04053 - 1.3931 \times 10^{-4}T - 9.23975 \times 10^{-9}T^2 + \\ + 0.544124/T)/A)(A - BT). \quad (6)$$

Values of $E^\circ_{(1)}$ and $E^\circ_{(2)}$ are given in Table I together with the difference $\Delta = E^\circ_{(2)} - E^\circ_{(1)}$. As can be seen, the standard potential difference of the electrosynthesis of peroxodisulfates by anodic discharge of sulfate ions is by about 0.1–0.15 V lower than the discharge of hydrogen sulfate ions at all considered temperatures and, in addition, it decreases with increasing temperature almost three times faster than the discharge of hydrogen sulfate ions. Therefore, of a purely thermodynamic point of view, the anodic discharge of sulfate ions at standard conditions should be the more preferred reaction, especially at higher temperatures. Of course, the actual participation of both anions on the electrosynthesis of peroxodisulfates is influenced not only by thermodynamic, but also by kinetic parameters of individual discharge reactions under real reaction conditions, the true detailed reaction mechanism of which has not been completely resolved[8,9], and the discussion of which does not form the subject of this contribution. A small difference in the now used value of the Faraday constant[10]

TABLE I
Standard potentials of the couples $S_2O_8^{2-}/SO_4^{2-}$ ($E^\circ_{(1)}$) and $S_2O_8^{2-}/HSO_4^{-}$ ($E^\circ_{(2)}$) in the temperature range 0–50 °C, and values of $\Delta = E^\circ_{(2)} - E^\circ_{(1)}$

Parameter	t, °C						
	0	10	20	25	30	40	50
$E^\circ_{(1)}$, V	1.9796	1.9640	1.9475	1.9389	1.9302	1.9120	1.8929
$E^\circ_{(2)}$, V	2.0712	2.0655	2.0598	2.0569	2.0540	2.0483	2.0425
Δ, V	0.0916	0.1015	0.1123	0.1180	0.1238	0.1363	0.1496

(96485.309 C mol^{-1}) against the previous one (96487.0 C mol^{-1}) used in ref.[4] had no substantial influence on the values of $E°_{(1)}$ and $E°_{(2)}$.

To evaluate the thermodynamics and kinetics of the electrosynthesis of peroxodisulfates under real reaction conditions, it is necessary to know the reversible potentials of anodic and cathodic electrode reactions as well, from which the anodic potential of the formation of peroxodisulfate ions almost exclusively determines the total reversible voltage of the electrosynthesis of peroxodisulfates. It is determined by the composition of the final anolyte flowing out from the anodic compartment of a continuously processing electrolyzer, containing not only the peroxodisulfate ions, but also some portion of the not converted sulfate ions. The following treatment is based on the commonly accepted presumption about the full dissociation of all considered strong electrolytes in their aqueous solutions. Expressing the molar ratio between the molality of M_2SO_4 (m_o) and H_2SO_4 (n) in the initial solution as $p = n/m_o$ and the conversion degree of M_2SO_4 to $M_2S_2O_8$ as α, then the molality of individual components in the final anolyte solution (neglecting the simultaneously proceeding anodic evolution of gaseous oxygen which does not determine the anodic potential of the formation of peroxodisulfate ions) is the following: molality of $S_2O_8^{2-}$ ions $m_2 = \alpha m_o$, remaining molality of SO_4^{2-} ions $m_1 = (1 + p - 2\alpha)m_o$ and remaining molality of H_2SO_4 $m_3 = (p - \alpha)m_o$. The overall reaction equation is expressed by the following relation

$$\begin{gathered} m_o\ M_2SO_4 + pm_o\ H_2SO_4 \pm 2\alpha m_o Fe = \\ \alpha m_o\ M_2S_2O_8 + (1 - \alpha)m_o\ M_2SO_4 + (p - \alpha)m_o\ H_2SO_4 + \alpha m_o\ H_2\ . \end{gathered} \tag{7}$$

As the electrosynthesis of peroxodisulfates usually proceeds at the atmospheric pressure, the fugacity coefficient of gaseous hydrogen can be taken as 1.0 and its activity as equal to its partial pressure $P(H_2)$ (in bar). The reversible anodic potential (versus reversible hydrogen electrode, RHE) of the electrosynthesis of peroxodisulfate is then given by the following expression

$$E_r = E°_{(1)} + (RT/(2F))\ \ln\ (\alpha\gamma_1 P(H_2)/((1 + p - 2\alpha)^2\gamma_2^2 m_o)) \tag{8}$$

where γ_1 and γ_2 are the mean activity coefficients of peroxodisulfate and sulfate ions in the final polycomponent anolyte solutions, respectively. At first, the idealized values of the reversible voltage E_r' were calculated for the simplifying assumptions $P(H_2) = 1.0$ bar and $\gamma_1 = \gamma_2 = 1.0$. These values for a wide possible range of parameters m_o, p, α and t (without any respect

TABLE II
Reversible anodic potentials of the electrosynthesis of peroxodisulfate solutions prepared at selected values of parameters m_o, p, α and t, assuming $P(H_2)$ = 1.0 bar and $\gamma_1 = \gamma_2 = 1.0$

p	α	E_r', V at m_o, mol kg^{-1}					
		0.1	0.5	1.0	2.0	4.0	6.0
				10 °C			
1.0	0.5	1.9836	1.9640	1.9555	1.9471	1.9386	1.9337
	0.7	2.0002	1.9806	1.9721	1.9637	1.9552	1.9503
	0.9	2.0301	2.0104	2.0020	1.9935	1.9851	1.9801
1.5	0.5	1.9737	1.9541	1.9457	1.9372	1.9287	1.9238
	0.7	1.9854	1.9658	1.9573	1.9489	1.9404	1.9355
	0.9	1.9995	1.9799	1.9714	1.9630	1.9545	1.9496
2.0	0.5	1.9667	1.9471	1.9386	1.9302	1.9217	1.9168
	0.7	1.9763	1.9556	1.9482	1.9397	1.9313	1.9263
	0.9	1.9864	1.9667	1.9583	1.9498	1.9414	1.9364
				25 °C			
1.0	0.5	1.9596	1.9389	1.9300	1.9211	1.9122	1.9070
	0.7	1.9770	1.9563	1.9474	1.9385	1.9296	1.9244
	0.9	2.0085	1.9878	1.9789	1.9700	1.9611	1.9559
1.5	0.5	1.9492	1.9285	1.9196	1.9107	1.9018	1.8966
	0.7	1.9614	1.9408	1.9319	1.9230	1.9141	1.9089
	0.9	1.9763	1.9556	1.9467	1.9378	1.9289	1.9237
2.0	0.5	1.9418	1.9211	1.9122	1.9033	1.8944	1.8892
	0.7	1.9518	1.9311	1.9222	1.9133	1.9044	1.8992
	0.9	1.9624	1.9418	1.9329	1.9240	1.9151	1.9098
				40 °C			
1.0	0.5	1.9330	1.9120	1.9029	1.8939	1.8694	1.8641
	0.7	1.9508	1.9297	1.9207	1.9116	1.9026	1.8973
	0.9	1.9827	1.9617	1.9527	1.9436	1.9346	1.9293
1.5	0.5	1.9224	1.9014	1.8924	1.8833	1.8742	1.8690
	0.7	1.9349	1.9139	1.9049	1.8957	1.8867	1.8814
	0.9	1.9500	1.9290	1.9199	1.9109	1.9018	1.8965
2.0	0.5	1.9149	1.8939	1.8848	1.8758	1.8667	1.8614
	0.7	1.9251	1.9041	1.8951	1.8860	1.8770	1.8717
	0.9	1.9359	1.9149	1.9059	1.8968	1.8878	1.8825

to solubility limitations) are given in Table II. As can be seen, values E_r' decrease with the increasing initial molality m_o of M_2SO_4, molar ratio p and temperature, and increase with the increasing conversion degree α. From these results and from the analysis of the appropriate solubility data[11,12], it follows that optimum conditions of the electrosynthesis of peroxodisulfates occur in such cases when the final anolyte composition approaches very closely to the solution saturated with the corresponding peroxodisulfate at the given temperature. Therefore, as an example, the electrosynthesis of an almost saturated solution of ammonium peroxodisulfate, suitable for its subsequent isolation by the crystallization, has been chosen, where it is suitable when the final anolyte does not contain any rest amount of free sulfuric acid, i.e. when $n = \alpha m_o$ and $p = \alpha$. In this case, the reversible anodic potential (vs RHE) is given by the equation

TABLE III

Reversible anodic potentials E_r of the electrosynthesis of almost saturated solutions of ammonium peroxodisulfate at various temperatures, conversion degree α and corresponding values of γ_1 and γ_2 at $P(H_2)$ = 1.0 bar; values of E_r' for $\gamma_1 = \gamma_2 = 1.0$ and values of $\Delta' = E_r - E_r'$

α	m_1 mol kg^{-1}	γ_1	m_2 mol kg^{-1}	γ_2	$E_{r(1)}$ V	E_r' V	Δ' V
				10 °C			
0.5	1.933	0.106	1.933	0.127	1.9789	1.9560	0.0229
0.7	2.418	0.107	1.036	0.133	1.9959	1.9739	0.0223
0.9	2.815	0.108	0.313	0.138	2.0261	2.0050	0.0212
				20 °C			
0.5	2.158	0.113	2.158	0.131	1.9616	1.9378	0.0238
0.7	2.739	0.114	1.174	0.137	1.9790	1.9562	0.0228
0.9	3.305	0.115	0.367	0.142	2.0099	1.9879	0.0220
				30 °C			
0.5	2.605	0.121	2.605	0.132	1.9430	1.9177	0.0253
0.7	3.265	0.122	1.399	0.139	1.9610	1.9369	0.0241
0.9	3.840	0.123	0.427	0.146	1.9929	1.9700	0.0229
				40 °C			
0.5	2.985	0.127	2.985	0.132	1.9240	1.8972	0.0268
0.7	3.724	0.129	1.596	0.140	1.9425	1.9171	0.0254
0.9	4.372	0.131	0.486	0.148	1.9755	1.9514	0.0241

$$E_{r(1)} = E^\circ_{(1)} + (RT/(2F)) \ln (m_1\gamma_1 P(H_2)/(m_2^2\gamma_2^2)) \qquad (9)$$

where $m_1 = \alpha m_o$ and $m_2 = (1 - \alpha)m_o$. Values m_1 and m_2 at the given values of α were determined from the solubility diagram of the system $(NH_4)_2S_2O_8$–$(NH_4)_2SO_4$–H_2O [13]. Values of the corresponding mean activity coefficients γ_1 and γ_2 were deduced from the results of the previous contribution[7]. Values of the reversible anodic potentials of the electrosynthesis of ammonium peroxodisulfate for the final anolyte composition at the temperature range 10–40 °C, conversion degree $\alpha = 0.5$–0.9 and for $P(H_2) = 1$ bar are given in Table III. In order to show the effect of activity coefficients on real values of the reversible anodic potential $E_{r(1)}$, values of the idealized reversible anodic potential $E_{r(1)}'$ (for $P(H_2) = 1.0$ bar and $\gamma_1 = \gamma_2 = 1$) and values of $\Delta' = E_{r(1)} - E'_{r(1)}$ are simultaneously given in Table III as well.

As can be seen, the increasing conversion degree α from 0.5 to 0.9 increases the reversible anodic potential $E_{r(1)}$ of the peroxodisulfate formation by 0.047–0.052 V, whereby the differences at lower temperatures are lower. The quite small difference of $\Delta' = 21$–27 mV for the considered range of individual parameters led to the conclusion that for the informative calculation of the reversible potential difference of the electrosynthesis of ammonium peroxodisulfate, it could be sufficient to only consider the concentrations of the reaction components in the final anolyte and to neglect their actual activity coefficients. An analogous conclusion was also deduced from the calculation of the reversible anodic potentials of the electrosynthesis of almost saturated solutions of sodium peroxodisulfate at various values of parameters m_o, p, α and t, using data[7,12,14].

If the same conclusion could be made for the reversible anodic potentials of the electrosynthesis of peroxodisulfates from diluted solutions, there are hitherto lacking values of the activity coefficients of reaction components in the appropriate diluted polycomponent systems. Nevertheless, due to the fact that the mean activity coefficients of $S_2O_8^{2-}$ and SO_4^{2-} ions at the given total ionic strength are not significantly different[15], it is very probable that the same conclusion could be applied for diluted solutions with a sufficient reliability as well.

CONCLUSION

It can be concluded that this work brings sufficiently reliable results of the calculation of the standard potentials of the couples $S_2O_8^{2-}/SO_4^{2-}$ and $S_2O_8^{2-}/HSO_4^-$ in the temperature range 0–50 °C and reversible values of the anodic potentials of the electrosynthesis of almost saturated solutions of ammonium peroxodisulfate solutions at various values of the initial molality of M_2SO_4 (m_o) and H_2SO_4 (n), their molar ratio $p = n/m_o = 1.0–2.0$ and conversion degree of sulfate to peroxodisulfate $\alpha = 0.5–0.9$ in the temperature range of 10–40 °C. The mean deviation of all presented anodic potentials can be estimated as ±5 mV. Nevertheless, the results of this study represent an important enhancement of the knowledge of standard and reversible thermodynamic data of peroxodisulfates in the temperature range 0–50 °C, applicable not only to the electrolytic processes but also to all electrochemical and chemical reactions of peroxodisulfates.

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REFERENCES

1. Machu W.: *Das Wasserstoffperoxyd und die Perverbindungen,* 2nd ed., Springer, Wien 1951.
2. Schumb W. C., Satterfield C. N., Wentworth R. L.: *Hydrogen Peroxide.* Reinhold, New York 1955.
3. Bertsch-Frank B., Engel D., Kleinschmit P., Lehmann T., Panster P., Steiner N., Jakobi S.: *Ullmann's Encyclopedia of Industrial Chemistry,* 6th ed., Vol. 25. Wiley VCH, Weinheim 2003.
4. Balej J.: *Electrochim. Acta* **1984**, *29*, 1239.
5. Wagman D. D., Evans W. H., Parker V. B., Schumm R. H., Halow I., Bailey S. M., Churney K. L., Nuttall R. L.: *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.
6. Balej J.: *Z. Phys. Chem.* **2010**, *224*, 883.
7. Balej J.: *Acta Chim. Slovaca* **2011**, *4*, 78.
8. Balej J., Matschiner H., Thiele W.: *Chem. Technik* **1978**, *29*, 1.
9. Serrano K., Michaud K. P. A., Comninellis C., Savall A.: *Electrochim. Acta* **2002**, *48*, 431.
10. Mills I., Cvitaš T., Homann K., Kallay N., Kuchitsu K.: *Quantities, Units and Symbols in Physical Chemistry*. IUPAC, Blackwell, Oxford 1988.
11. Balej J.: *Collect. Czech. Chem. Commun.* **1965**, *30*, 2663.
12. Balej J.: *Collect. Czech. Chem. Commun.* **1970**, *35*, 1954.
13. Balej J., Regner A.: *Collect. Czech. Chem. Commun.* **1963**, *28*, 1266.
14. Balej J., Regner A.: *Collect. Czech. Chem. Commun.* **1967**, *32*, 4491.
15. Balej J.: *Acta Chim. Slovaca* **2011**, *4*, 68.