Mean Activity Coefficients of Aqueous Solutions of Peroxodisulfates at 0 – 50 °C

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Abstract

Activity coefficients of aqueous saturated solutions of sodium, potassium and ammonium peroxodisulfates at 0 – 50 °C have been derived on the basis of the thermodynamic equilibrium condition between the solid substance and its saturated solution. Suitable relations for the dependence of the activity coefficients on the temperature have been derived. For the estimation of activity coefficients of diluted solutions, the method according to Bromley has been applied for potassium peroxodisulfate solutions and according to Meissner for sodium and ammonium peroxodisulfate solutions.

Keywords: activity coefficient, Sodium peroxodisulfate, Potassium peroxodisulfate, Ammonium peroxodisulfate, Bromley´s method, Meissner´s method

Introduction

In the previous contribution (Balej 2010), lacking data of $\Delta_f H°$, $\Delta_f G°$, $S°$ and $C°_p$ of solid and aqueous sodium, potassium and ammonium peroxodisulfate, simultaneously with activity coefficients of their saturated solutions at 25 °C have been estimated. Furthermore, using suitable estimation methods for the temperature dependence of the $C°_p$ data, the corresponding values of $\Delta_f H°$ and $\Delta_f G°$ of sodium, potassium and ammonium peroxodisulfates in the standard solid and aqueous state at 0 – 50 °C have been derived. For the serious evaluation of thermodynamic and kinetic data of the electrosynthesis and other chemical and electrochemical reactions of peroxodisulfates, it is further necessary to know the activity coefficients of these substances in the corresponding systems, especially in solutions near to the saturation. However, only few not reliable data of activity coefficients of diluted solutions of sodium, rubidium and cesium peroxodisulfates are available (Goldberg 1981). They have

been calculated from the experimentally determined osmotic coefficients. Osmotic coefficients of saturated solutions of sodium and potassium peroxodisulfates (Apelblat et al. 2001) and ammonium peroxodisulfates (Apelblat and Korin 2003) have recently been measured at 278.15 – 323.15 K, however, corresponding activity coefficients have not been given. Consequently, reliable data of activity coefficients of sodium, potassium and ammonium peroxodisulfate solutions are always lacking, evidently due to two reasons: a) it is impossible to directly measure the reversible potential of the electrode $S_2O_8^{2-}/SO_4^{2-}$ or $S_2O_8^{2-}/HSO_4^{-}$, because it is impossible to realize an inert electrode indicating only the potentials of these redox systems the reversibility of which has never been proved, and b) aqueous peroxodisulfate ions can decompose into sulfate and/or hydrogen sulfate ions during the long time equilibration of the measured system, so that the measured potential can be disturbed by the presence of other components. Some activity coefficients of saturated solutions of ammonium peroxodisulfate in aqueous binary and polycomponent systems at 20 °C have been derived (Vilcu et al. 1980, 1981, 1982) from the solubility data (Balej 1965), but they are not reliable enough due to some reasons: a) values of osmotic coefficients φ_{CaCl2} for $m = 0.1 - 3.0$ mol kg^{-1} at 0 °C, used as reference data in paper (Vilcu and Irinei 1982), differ distinctly from the reliable values (Platford 1973); b) data of osmotic coefficients $\varphi_{(NH4)2SO4}$ for $m = 0.1 - 3.0$ mol kg^{-1} at 0 °C (Vilcu et al. 1981) differ quite distinctly from those (Apelblat and Korin 2003); c) some data (Vilcu et al. 1980) are incorrect as they refer to ammonium sulfate and not to ammonium peroxodisulfate as the coexisting solid phase.

In the previous paper (Balej 2010), the activity coefficients of the saturated solutions of sodium, potassium and ammonium peroxodisulfates at 25 °C have been calculated on the basis of the thermodynamic condition for the equilibrium between the solid substance and its saturated solution. The same relation has now been used for the calculation of activity coefficients of saturated solutions of the same peroxodisulfates at 0 – 50 °C. In order to extend the knowledge of activity coefficients of peroxodisulfates to more diluted solutions in the whole considered temperature range, a combination of the now presented data for saturated solutions with suitable estimation methods has been tried. All calculations have been performed under the commonly accepted presumption of a complete dissociation of the considered strong electrolytes.

Results and Discussion

The expression for the calculation of the activity coefficient of saturated aqueous solution of strong uni-bivalent electrolyte was derived from the thermodynamic condition of the equilibrium between the solid electrolyte, $C_2A(cr)$, and its saturated coefficient of saturated aqueous solution of strong uni-bivalent electrolyte was derived from the thermodynamic condition of the equilibrium between the solid electrolyte, $C_2A(cr)$, and its saturated solution, and is formulated (Balej 2010) by the equation

$$\ln \gamma_s = ((\Delta_f G°_{cr} - \Delta_f G°_{aq})/(RT) - \ln (4m_s^3))/3 \tag{1}$$

Here, $\Delta_f G°_{cr}$ and $\Delta_f G°_{aq}$ denotes the standard formation Gibbs energy of the considered electrolyte in the solid state and the standard aqueous solution, respectively, m_s and γ_s represents molality and mean activity coefficient of the saturated solution at the given temperature. Values of $\Delta_f G°_{cr}$ and $\Delta_f G°_{aq}$ of the considered peroxodisulfate in the temperature range 0 - 50 °C have been taken from the previous paper (Balej 2010). For corresponding solubilities, there were available on one hand own data for all considered peroxodisulfates (Balej and Regner 1963, 1960, 1966), on the other hand recent data for sodium and potassium salt (Apelblat et al. 2001). Between corresponding results, there exists a sufficient agreement with a maximum deviation 1.9 rel. % at sodium salt, and 2.7 rel. % at potassium salt. For the evaluation of activity coefficients of saturated sodium and potassium peroxodisulfate solutions, values obtained by a common correlation of data of both sources have been used, which could be expressed by the following relations:

for sodium salt

$$\ln m_s = 3.33953 - 660.490 / T \tag{2}$$

and for potassium salt

$$\ln m_s = 11.9193 - 4003.47 / T \tag{3}$$

The values of activity coefficients of saturated solutions of the considered peroxodisulfates for the temperature range 0 – 50 °C are given in Table 1. In the case of sodium and ammonium peroxodisulfate, activity coefficients of their saturated solutions continually increase with increasing temperature, while in the case of potassium salt the corresponding dependence is opposite. In this case, due to the low solubility of this salt changing from 0.065 to 0.630 mol kg^{-1} in the range 0 – 50 °C corresponding γ_s data evidently lie in the region where the influence of the increasing concentration causing a decrease of the

activity coefficient is prevailing. On the other hand, in the case of sodium and ammonium peroxodisulfate with solubilities in the range 2.4 – 5.2 mol kg^{-1}, the increase of activity coefficients of saturated solutions with increasing temperature can evidently be ascribed to the positive influence of temperature on the activity coefficients and on the solubility as well. As can also be seen, the present value of the activity coefficient of the saturated solution of ammonium peroxodisulfate at 20 °C, $\gamma_s = 0.116$, is distinctly lower than the value $\gamma_s = 0.298$ (Vilcu et al. 1980).

Table 1. Mean activity coefficients of saturated aqueous solutions of sodium, potassium and ammonium peroxodisulfate in the temperature range 0 – 50 °C.

t [°C]	$Na_2S_2O_8$		$K_2S_2O_8$		$(NH_4)_2S_2O_8$	
	m_s	γ_s	m_s	γ_s	m_s	γ_s
0	2.5130	0.111	0.0647	0.508	2.4383	0.105
5	2.6247	0.117	0.0843	0.465	2.7165	0.107
10	2.7370	0.123	0.1086	0.421	2.9947	0.110
15	2.8501	0.127	0.1388	0.393	3.2729	0.113
20	2.9637	0.133	0.1760	0.363	3.5511	0.116
25	3.0779	0.139	0.2213	0.336	3.8293	0.120
30	3.1924	0.145	0.2761	0.313	4.1075	0.124
35	3.3073	0.151	0.3421	0.291	4.3857	0.128
40	3.4224	0.157	0.4210	0.272	4.6639	0.133
45	3.5378	0.163	0.5146	0.255	4.9421	0.138
50	3.6533	0.171	0.6253	0.240	5.2203	0.143

The temperature dependence of activity coefficients of saturated solutions of the considered peroxodisulfates in the given temperature range could be expressed with a sufficient agreement by the following expressions:
for sodium salt:

$$\ln \gamma_s = 0.520635 - 742.722 / T \qquad (4)$$

for potassium salt:

$$\ln \gamma_\text{s} = -5.51950 + 1321.132 / T \tag{5}$$

and for ammonium salt:

$$\ln \gamma_\text{s} = -0.28806 - 544.161 / T \tag{6}$$

To calculate the course of chemical and electrochemical reactions under participation of peroxodisulfates at various reaction conditions, the knowledge of activity coefficients of these substances at lower concentrations is of the same importance. While the activity coefficients of corresponding sulfates are known with sufficient accuracy in the whole range from very diluted up to the saturated or even supersaturated solutions (Goldberg 1981, Robinson and Stokes 1955, Harned and Owen 1958, Harned and Hecker 1934, Scatchard and Prentiss 1932, Wishaw and Stokes 1954, Rogers and Pitzer 1981, Clegg et al. 1996, Rard et al. 2000, Archer and Kirklin 2002, Palmer et al. 2002, El Guendouzi et al. 2003), data of peroxodisulfates (with the exception of the above mentioned less reliable data of diluted solutions of sodium, rubidium and cesium salts (Goldberg 1981) are lacking. Their approximative estimation, however, could now be possible on the basis of the derived values of activity coefficients of saturated solutions. For this purpose, a one-parameter equation (Bromley 1973) representing a suitably adapted extended Debye-Hückel equation could be considered. Its common expression adapted for a 1-2 electrolyte and valid for ionic strength $I_\text{i} = 0.5\Sigma m_\text{i}z_\text{i}^2 \leq 6 \text{ mol kg}^{-1}$

$$\log \gamma = -2A_\gamma(3m)^{0.5}/(1 + (3m)^{0.5}) + (0.36m + 3.6Bm)/(1 + 2.25m)^2 + 3Bm \tag{7}$$

allows the calculation of the probable values of activity coefficient, knowing the temperature depending value of parameter B specific for the given electrolyte. Its value can be obtained for the known γ_s at the given m_s from the expression

$$B = (\log \gamma_\text{s} + 2A_\gamma(3m_\text{s})^{0.5}/(1+ (3m_\text{s})^{0.5}) - 0.36m_\text{s}/(1+2.25m_\text{s})^2)/(3m_\text{s}+3.6m_\text{s}/(1+2.25m_\text{s})^2 \tag{8}$$

Values of the temperature depending Debye-Hückel coefficient A_γ have been taken from (Pitzer 1991). However, an important fact has not been mentioned by Bromley, namely that the parameter B for the given electrolyte is mostly also concentration depending, because its different values can be obtained from Eq. (8) using values of γ at different values of m. Consequently, values B for various electrolytes at 25 °C given by Bromley only express some average value the exact determination method of them has unfortunately not been given.

However, as has now been ascertained for the case of potassium sulfate, its value $B = -0.032$ kg mol^{-1} at 25 °C (Bromley 1973) is close to the value for the saturated solution. Other forms of the extended Debye-Hückel equations always containing more parameters (e.g. Pitzer equation (Pitzer 1991)) did not come into consideration.

Eq. (7), due to its validity limitation, could only be applied to solutions of potassium peroxodisulfates with $m_s < 2$ mol kg^{-1} in the whole considered temperature range, for sodium and ammonium peroxodisulfate solutions with $m_s > 2$ mol kg^{-1}, it could not be applied. Values of parameter B of potassium peroxodisulfate solutions for the considered temperature range calculated from Eq. (8) (see Table 2) are negative (similarly as for potassium sulfate (see above)), with a distinct minimum at ca. 17 °C. Values of activity coefficients of potassium peroxodisulfate at $0.01 \leq m < m_s$ obtained for the considered temperature range are presented in Table 3. As can be seen, they continually decrease with increasing molality and temperature which is caused by the same reasons as at the temperature dependence of activity coefficients of saturated solutions of this salt (see above). The reliability of the given results can be checked only indirectly by comparing values of activity coefficients of e.g. potassium sulfate derived at $m = 0.1$ and 0.5 mol kg^{-1} and 25 °C by Bromley method ($\gamma = 0.4423$ and 0.2616) with recent very reliable values (Palmer et al. 2002), ($\gamma = 0.4388$ and 0.2610). As can be seen, a very good agreement between calculated and experimental can be observed. Comparing further some calculated values of activity coefficients of potassium peroxodisulfate by Bromley method at 0, 25 and 50 °C (see Table 3) with corresponding values of potassium sulfate at the same molality (Palmer et al. 2002), one can see a satisfactory closeness in both series. This confirms the previous assumption (Balej 2010) about the quite close values of activity coefficients of peroxodisulfate and sulfate solutions with the same cation at the same molality.

Table 2. Values of parameter B of peroxodisulfate solutions calculated using equation (8).

t [°C]	0	10	20	25	30	40	50
B [mol kg^{-1}]	−0.03975	−0.06194	−0.05759	−0.05176	−0.04521	−0.03150	−0.01922

Table 3. Activity coefficients of potassium peroxodisulfate calculated using Eq. (7).

m [mol kg^{-1}]	γ at t °C						
	0	10	20	25	30	40	50
0.01	0.717	0.713	0.708	0.707	0.705	0.701	0.696
0.02	0.641	0.637	0.632	0.630	0.628	0.623	0.617
0.05	0.533	0.526	0.521	0.519	0.516	0.511	0.505
0.10	--	0.438	0.437	0.435	0.432	0.427	0.422
0.15	--	--	0.390	0.388	0.385	0.381	0.376
0.20	--	--	--	0.356	0.354	0.350	0.345
0.30	--	--	--	--	--	0.308	0.304
0.40	--	--	--	--	--	0.281	0.278
0.50	--	--	--	--	--	--	0.258
0.60	--	--	--	--	--	--	0.244

For solutions of sodium and ammonium peroxodisulfates with $m_s > 2$ mol kg^{-1}, no suitable one-parameter method is available for the estimation of activity coefficients of their diluted solutions. Therefore, a graphical method (Meissner et al. 1972 a, b, 1980) applicable for the range $I \leq 100$ mol kg^{-1} came into consideration. It is based on the discovery that the isothermal logarithmic plot of the reduced activity coefficient log Γ vs. log I for electrolytes of various types ($\Gamma = \gamma^{1/2}$ for 1-2 electrolytes) forms a system of mutually not crossing curves enabling the estimation of the course of this dependence on the basis of a known value of γ at a known value of I, independent on temperature. However, the verification of this method using reliable data for sodium (Rard et al. 2000) and ammonium sulfates (Clegg et al. 1996) has shown that the course of these data does not sufficiently coincide with the general plot log Γ vs. log I after Meissner. Therefore, a special plot log Γ vs. log I was constructed using reliable data of sodium and ammonium sulfates which should exhibit a close course to the corresponding peroxodisulfate solutions (Kielland 1937). Values of activity coefficients of sodium and ammonium peroxodisulfate were then estimated from these plots, using known values of activity coefficients of the given peroxodisulfate in its saturated solutions at the given temperature as the basic points.

Table 4. Activity coefficients of sodium peroxodisulfate solutions obtained by combination of presented data of saturated solutions and the modified Meissner´s method.

m [mol kg^{-1}]	γ at t °C						
	0	10	20	25	30	40	50
0.1	0.442	0.445	0.448	0.449	0.451	0.453	0.455
0.2	0.353	0.359	0.365	0.368	0.370	0.374	0.378
0.3	0.304	0.315	0.320	0.323	0.329	0.335	0.341
0.5	0.244	0.255	0.264	0.269	0.272	0.282	0.290
0.7	0.207	0.219	0.229	0.237	0.239	0.250	0.260
1.0	0.172	0.185	0.196	0.205	0.207	0.219	0.230
1.5	0.139	0.152	0.165	0.173	0.177	0.191	0.202
2.0	0.122	0.136	0.148	0.155	0.161	0.175	0.187
2.5	0.112	0.126	0.139	0.145	0.152	0.166	0.180
3.0	--	--	--	0.139	0.146	0.159	0.174
3.5	--	--	--	--	--	--	0.172

Estimated values of activity coefficients of sodium and ammonium peroxodisulfate solutions for selected molalities $0.1 \leq m < m_s$ in the considered temperature range are summarized in Table 4 and 5. As can be seen, the activity coefficients of both salts at the given molality increase almost linearly with increasing temperature, while activity coefficients of corresponding sulfates exhibit flat maxima shifting to higher temperatures with increasing solution concentration (Rard et al. 2000, Clegg et al. 1996). Consequently, quite good closeness can be observed between activity coefficients of corresponding peroxodisulfate and sulfate solutions of the same concentration in the temperature range $0 – 25$ °C, while at higher temperatures, the difference between both values begins to increase. As the data only represent estimated and not measured values, no correlation equations have been derived, but the estimated data enable quite simple interpolation in the considered molality and temperature range. Due to the impossibility to ascertain exact mean deviations of the activity coefficients of saturated solutions of individual considered peroxodisulfates, only an overall value of the common mean deviation $\sigma \leq 0.01$ of all presented data can be estimated for the considered concentration and temperature range.

Table 5. Activity coefficient of ammonium peroxodisulfate solutions obtained by combination of presented data of saturated solutions and the modified Meissner´s method.

m [mol kg^{-1}]	γ at t °C						
	0	10	20	25	30	40	50
0.1	0.432	0.436	0.440	0.442	0.444	0.448	0.453
0.2	0.330	0.338	0.348	0.351	0.355	0.365	0.375
0.3	0.280	0.290	0.299	0.304	0.309	0.316	0.325
0.5	0.226	0.238	0.247	0.252	0.256	0.267	0.277
0.7	0.198	0.208	0.217	0.222	0.226	0.236	0.246
1.0	0.168	0.178	0.187	0.191	0.195	0.205	0.215
1.5	0.137	0.148	0.157	0.161	0.166	0.176	0.185
2.0	0.117	0.128	0.138	0.144	0.149	0.160	0.170
2.5	--	0.116	0.126	0.131	0.136	0.148	0.158
3.0	--	0.108	0.119	0.125	0.130	0.141	0.152
3.5	--	--	0.115	0.121	0.124	0.136	0.149
4.0	--	--	--	--	0.123	0.136	0.149
4.5	--	--	--	--	--	0.133	0.144
5.0	--	--	--	--	--	--	0.142

Conclusion

With the respect to the fact that up today, no values of activity coefficients of aqueous solutions of sodium, potassium and ammonium peroxodisulfates have directly been measured, it can be concluded that the present results obtained by suitable estimation methods provide sufficiently reliable values of the activity coefficients of the considered peroxodisulfates in both saturated and diluted solutions important for theoretical and technical calculations of all chemical and electrochemical processes under participation of these substances. This contribution could also give a new impulse to the direct experimental measurement of activity coefficients of peroxodisulfates using modern experimental techniques.

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