

Solubility in the System $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{—NH}_3\text{—H}_2\text{O}$ and Mean Activity Coefficients of Saturated Solutions of $(\text{NH}_4)_2\text{S}_2\text{O}_8$

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Abstract: The solubility data of ammonium peroxodisulfate in aqueous ammonia solutions at 15.5 °C have been evaluated using the relative activity coefficient expansion. Using the known value of the mean activity coefficient of saturated solution of ammonium peroxodisulfate in pure water, values of the mean activity coefficients of this salt in the saturated solutions of the given system have been calculated.

Keywords: Solubility, Ammonium peroxodisulfate, Ammonia, Activity coefficients

Introduction

In the previous paper (Balej 1982), the correlation of the solubility data in aqueous ternary systems containing sodium, potassium and ammonium peroxodisulfates have been presented. Here, among others, correlation equations of solubilities in the following ternary systems with common cations have been evaluated: $\text{Na}_2\text{S}_2\text{O}_8\text{—Na}_2\text{SO}_4\text{—H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_8\text{—NaOH—H}_2\text{O}$, $\text{K}_2\text{S}_2\text{O}_8\text{—K}_2\text{SO}_4\text{—H}_2\text{O}$, $\text{K}_2\text{S}_2\text{O}_8\text{—KOH—H}_2\text{O}$, and $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{—}(\text{NH}_4)_2\text{SO}_4\text{—H}_2\text{O}$. These results have recently been used (Balej 2011) for the evaluation of the activity coefficients of the considered peroxodisulfates in the appropriate saturated ternary solutions. Solubility data in the analogous ternary system $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{—NH}_3\text{—H}_2\text{O}$ presented in the literature (Weitz and Stamm 1925) in a graphical form are based on numerical data measured at 15.5 °C (Stamm 1926). They show a high increase in the solubility of this salt with the increasing concentration of aqueous ammonia, similarly as other ammonium salts of monobasic inorganic as well as organic acids (Weitz and Stamm 1925, Stamm 1926). The present paper brings some further informations about this system, especially values of the mean activity coefficients of ammonium peroxodisulfate in its saturated solutions.

Results and discussion

The solubility data of ammonium peroxodisulfate in aqueous ammonia solutions at 15.5 °C given in equivalent/100 g H_2O (Stamm 1926) and transformed into mol kg^{-1} are presented in Table 1. The total amount of the aqueous ammonia reaching up to 60 mol kg^{-1} was expressed as $\text{NH}_3(\text{aq})$ in the whole considered concentration range. This approach fully conforms with that

(Clegg and Brimblecombe 1989) dealing with the solubility of ammonia in pure aqueous and multi-component solutions under application of Pitzer thermodynamic model (Pitzer 1991). In this case, the individual forms of dissolved ammonia are determined by the equilibrium of the reaction



The temperature dependence of the equilibrium constant of reaction (1)

$$K_{(1)} = m_{\text{NH}_4^+} m_{\text{OH}^-} \gamma_{\text{NH}_4^+} \gamma_{\text{OH}^-} / (m_{\text{NH}_3} \gamma_{\text{NH}_3}) \quad (2)$$

$(m^\ominus = 1 \text{ mol kg}^{-1})$

at 0–40 °C is expressed (Clegg and Brimblecombe 1989) by the equation

$$\ln K_{(1)} = 16.9732 - 4411.023/T - 0.0440 T \quad (3)$$

$(m^\ominus = 1 \text{ mol kg}^{-1})$

so that $K_{(1)}(m^\ominus = 1 \text{ mol kg}^{-1}) = 1.655 \times 10^{-5}$ at 15.5 °C. From these data, it followed that in ammoniacal saturated solutions of ammonium peroxodisulfate with $m_s > 3.273 \text{ mol kg}^{-1}$ (under the usual presumption of its total dissociation), the dissociation degree of aqueous ammonia (with concentration up to ca. 60 mol kg^{-1}) reaches values in the order 10^{-6} to 10^{-7} . Therefore, the consideration that the total amount of aqueous ammonia in this system is present as molecular $\text{NH}_3(\text{aq})$ is fully justified. Accordingly, this system can be considered as a ternary system $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{—NH}_3\text{—H}_2\text{O}$ without a common ion.

The results of the evaluation procedure are summarized in Table 1. Comparing the measured solubility in pure water (3.28 mol kg^{-1}) with the own value (Balej and Regner 1966) at 15.5 °C (3.301 mol kg^{-1}), one can see a difference of 0.64 rel. %. The increasing content of aqueous ammonia, m_2 , enlarged very distinctly the solubility of ammonium peroxodisulfate which, at $m_2 \sim 60 \text{ mol kg}^{-1}$, reaches an almost five-fold higher value than in pure water. The

quantitative influence of ammonia on the solubility of ammonium peroxodisulfate at the given temperature was expressed using the relative activity coefficients expansion for a ternary system without common ions (Balej 1982)

$$\varphi = \log (\gamma_{10}/\gamma_1) = \log (m_{1s}/m_{1so}) = f(m_2) \quad (4)$$

leading, for $m_{1so} = 3.28 \text{ mol kg}^{-1}$, to the following expression

$$\log m_{1s} = 0.515874 + 0.015118 m_2 - 6.612 \times 10^{-5} m_2^2 \quad (5)$$

(see Table 1) with the mean deviation $\pm 0.42 \text{ rel. \%}$. Using $m_{1so} = 3.301 \text{ mol kg}^{-1}$ (Balej and Regner 1966) which is 0.64 rel. % higher than the value by Stamm, one obtains the following expression

$$\log m_{1s} = 0.518606 + 0.01484 m_2 - 6.1923 \times 10^{-5} m_2^2 \quad (6)$$

with a little lower mean deviation $\pm 0.21 \text{ rel. \%}$ (see Table 1).

From Eq. (4), the following expression can be obtained for the mean activity coefficients of ammonium peroxodisulfate in its saturated solutions for the whole measured concentration range of aqueous ammonia

$$\gamma_{1s} = \gamma_{1so} m_{1so}/m_{1s} = 0.373/m_{1s} \quad (7)$$

with $\gamma_{1so} = 0.113$ and $m_{1so} = 3.301 \text{ mol kg}^{-1}$ (Balej 2011). Values γ_{1s} are given in Table 1 as well. As can be seen, the quite low value of the mean activity coefficient of saturated solution of ammonium peroxodisulfate in pure water further decreases with increasing concentration of aqueous ammonia. This affection of the solubility and activity coefficient of ammonium peroxodisulfate by aqueous ammonia is totally opposite than in the system $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ where the increasing content of sulfuric acid in the saturated ternary solution causes the decrease of solubility and consequently the increase of activity coefficient of ammonium peroxodisulfate (Balej 1982, 2011). The elucidation of this fact does not form the aim of this contribution, nevertheless, due to its common importance, it deserves the attention of the corresponding specialists.

The solubility increase of ammonium salts caused by aqueous ammonia is a common property of

ammonium salts of monobasic inorganic as well as organic acids (Weitz and Stamm 1925, Stamm 1926), while the opposite behaviour is commonly observed at ammonium salts of dibasic acids. The fact that ammonium peroxodisulfate as salt of a dibasic acid does not obey this rule was explained (Weitz and Stamm 1925) by the circumstance that the peroxodisulfate ion is formed by a direct linkage of two monobasic groups —OSO_3^- , and in this way its ammonium salt behaves as a “twice monobasic” salt. The same behaviour has been observed at the solubility of similarly “twice monobasic” ammonium dithionate $(\text{NH}_4)_2\text{S}_4\text{O}_6$, where the anion is built by a direct linkage of two monobasic groups $\text{—S}_2\text{O}_5^-$ (Weitz and Stamm 1925).

The observed distinct increase of the solubility of monobasic ammonium salts by the increasing content of aqueous ammonia was explained by the formation of some ammo-complexes (Weitz and Stamm 1925), however, no concrete composition of such a complex for the given system has been given. The same assumption without further concrete ammo-complex composition was mentioned later (Clegg and Brimblecombe 1989). Therefore, the final solution of this problem must be obtained by a thorough experimental determination of the composition of both coexisting solid and saturated aqueous phases which, however, lies outside the present possibilities of the author.

Conclusion

It can be concluded that this contribution has brought a further extension of the knowledge of the solubility and activity coefficients of ammonium peroxodisulfate in aqueous polycomponent systems. It also brings some impulse for a further thorough measurement of solubility in this system in a wide range of concentration and temperature with clean composition determination of the coexisting solid and liquid phases which could be very important not only from the theoretical point of view, but could probably be utilized in different technological aspects of the usage of peroxodisulfates.

Tab. 1. Solubility of ammonium peroxodisulfate in aqueous ammonia and its mean activity coefficients at 15.5 °C.

NH_3 $m_2/\text{mol kg}^{-1}$	$(\text{NH}_4)_2\text{S}_2\text{O}_8$			γ_{1s}
	obs.	Eq. (5)	Eq. (6)	
0	3.28	3.28	3.301	0.113
11.63	4.82	4.82	4.82	0.077
41.10	10.54	10.61	10.57	0.035
59.20	15.19	15.11	15.14	0.024

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