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Research Article

Vapor Pressure of Saturated Aqueous Solutions of Potassium Sulfate from 310 K to 345 K

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The experimental evaluation of the vapor pressure of saturated aqueous solutions of potassium sulfate was carried out in the range of temperatures $310\,\mathrm{K} \leq T \leq 345\,\mathrm{K}$. The experimental data were used to determine the corresponding values of the water activity in such solutions. The analytical expressions as a function of temperature of both, vapor pressure and water activity, were obtained from the correlation of the experimental results. The vapor pressure expression was also extrapolated to a different temperature range in order to make a comparison with the results obtained by other authors.

1. Introduction

The dependence on temperature of the vapor pressure of saturated aqueous solutions has been already determined for most of the inorganic salts, particularly halides, sulfates, and nitrates [1–3]. However, for the case of potassium sulfate the available information is surprisingly scarce and restricted to the temperature range $273\,\mathrm{K} \leq T \leq 323\,\mathrm{K}$ [4–7] plus one evaluation at 374 K [8]. On this context, the present work studied experimentally the vapor pressure of saturated aqueous solutions of potassium sulfate from 310 K to 345 K and evaluated from these data the dependence of the water activity on temperature. For this purpose, an isothermal static apparatus has been constructed and the reliability of the methodology employed was verified through the determination of the vapor pressure of pure water.

2. Experimental Section

2.1. Equipment. The apparatus used for the vapor pressure measurements, which is a modified version of the device employed by Kim et al. [9], is shown in Figure 1. It consists of a round-bottom flask (A) of $125\,\mathrm{cm}^3$ which contains the solution to be evaluated. It is connected to a U-tube mercury manometer (F) and to a vacuum pump (H) through the valve (G). The flask, the manometer, and the connecting tubes are immersed in an isothermal water bath (B), which temperature is controlled by a Lauda Thermostat UB20 Ultra (E), thermostated to within $\pm 0.01\,\mathrm{K}$. To ensure the uniformity of the bath temperature, a recirculation pump (D) was used with a flow rate of $4\,\mathrm{dm}^3\,\mathrm{min}^{-1}$. Moreover, a magnetic stirrer (C) was used in order to ensure the highest mass transfer rate between the liquid and vapor phases and also the temperature uniformity inside the equilibration flask. The temperature was measured by a digital thermometer Lauda R46, with a Pt resistance of $100\,\Omega$ which precision is $\pm 0.01\,\mathrm{K}$. The pressure was measured by an open U-tube mercury manometer and the manometric readings were made with a cathetometer to $\pm 0.1\,\mathrm{mm}$ ($\pm 0.015\,\mathrm{kPa}$). The reading performed at the temperature of each experiment was corrected according to the thermal expansion coefficient of mercury [10] and referred to 273.15 K. The atmospheric pressure was measured by a calibrated barometer.

2.2. Reagents. Potassium sulfate was analytical grade reagent manufactured by Merck and was used in the experiments without further purifications. The solutions were prepared with ultra-pure water (PureLab, Elga LabWater). Solid K_2SO_4 and the saturated solutions were degassed at room

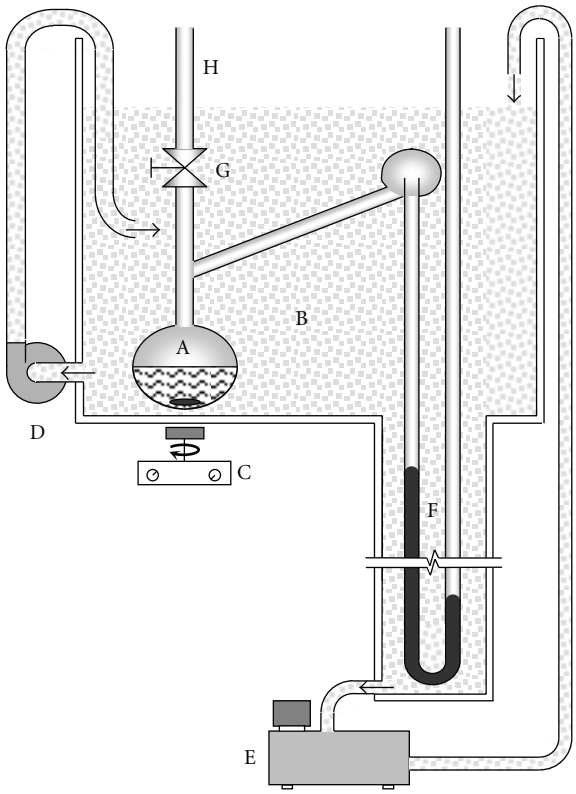

Figure 1: Device for vapor pressure measurements. (A) Equilibration flask; (B) isothermal water bath; (C) magnetic stirrer; (D) recirculation pump; (E) thermostat; (F) U-tube mercury manometer; (G) valve; (H) to condenser and vacuum pump.

temperature into a vacuum oven previously to be put into the equilibration flask.

2.3. Procedures. In each experiment, a volume of approximately 80 cm^3 of the saturated solution of potassium sulfate at room temperature was put into the flask (A) together with an amount of solid K_2SO_4, high enough to ensure the saturation condition at the temperature of the experiment, and a magnetic bar. Then the system was vacuumized through the valve (G) during two hours, with a vigorous and continuous agitation of the solution, ensuring that the boiling point is reached. This process produces the complete displacement of air by water vapor. After this stage, valve (G) is closed and the water bath (B) begins to be heated through the thermostat (E) and the recirculation pump (D). The solution is continually agitated to facilitate that the system could reach the equilibrium state, which is verified through the invariance of the manometric pressure. The presence of solid salt is also verified in order to ensure the saturation of the solution. In these conditions, the values of the temperature (T) and the vapor pressure (P_w) are obtained. The same procedure is used to verify the correct proper functioning of the equipment through the evaluation of the dependence of the vapor pressure of pure water on temperature.

Table 1: Measured and standard[(a)] values of vapor pressure of pure water and relative deviation.

T/K	P_w/kPa	$P_w^{s\,(a)}$/kPa	$(\Delta P_w/P_w^s) \times 100$
308.10	5.62	5.612	−0.140
313.35	7.46	7.465	0.067
318.70	9.87	9.870	0.000
323.2	12.38	12.382	0.016
327.95	15.63	15.612	−0.120
327.95	15.61	15.612	0.013
333.35	20.13	20.132	0.010
333.65	20.40	20.413	0.064
337.55	24.38	24.378	−0.008
338.00	24.87	24.875	0.020
338.05	24.93	24.931	0.004
338.25	25.15	25.155	0.020
343.80	32.06	32.089	0.090
348.45	39.12	39.083	−0.094
348.50	39.16	39.164	0.010
348.50	39.17	39.164	−0.015
353.25	47.61	47.607	−0.006
353.45	48.00	47.994	−0.012

[(a)] [11].

3. Results

3.1. Vapor Pressure of Pure Water. Before the evaluation of the vapor pressure of the saturated aqueous solution of K_2SO_4 at different temperatures, the dependence of the vapor pressure of pure water on temperature was measured in order to verify the adequate operation of the apparatus, through the comparison of the results obtained with values reported in the literature [8]. Table 1 shows the values of the vapor pressure of pure water ($P_w^{s(\mathrm{exp})}$) measured in the range $307\,\mathrm{K} \leq T \leq 353\,\mathrm{K}$. The corresponding values obtained from the correlation proposed by Wagner and Pruß [11] ($P_w^{s(\mathrm{ref})}$) are also illustrated. It can be appreciated that the average value of the relative deviation, evaluated as $(P_w^{s(\mathrm{exp})} - P_w^{s(\mathrm{ref})})100/P_w^{s(\mathrm{ref})}$, is 0.04%, while the highest value is 0.14%. These results demonstrate the correct functioning of the experimental device and the applied methodology.

3.2. Vapor Pressure of K_2SO_4-Saturated Solutions. Table 2 illustrates the values of the vapor pressure of saturated solutions of K_2SO_4 (P_w) measured at different temperatures. The relationship between $\ln P_w$ and the inverse of temperature is shown in Figure 2 (■). These experimental values were correlated employing the equation proposed by Apelblat and Korin [12], through the use of nonlinear least squares regression, and the resulting expression was as follows:

$$\ln(P_w/\mathrm{kPa}) = 23.22469 - \frac{5293.806}{(T/\mathrm{K})} - 0.75463\ln(T/\mathrm{K}). \tag{1}$$

This analytical dependence is illustrated in Figure 2 (continuous line). The quality of the correlation can be appreciated

Table 2: Vapor pressure and water activity of saturated aqueous solutions of potassium sulfate.

T/K	P_w/kPa	a_w
313.25	7.27	0.9787
313.65	7.43	0.9788
314.80	7.88	0.9768
315.95	8.56	0.9759
317.55	9.07	0.9741
318.75	9.63	0.9732
320.45	10.48	0.9710
321.60	11.08	0.9690
322.90	11.81	0.9682
323.25	12.02	0.9680
324.60	12.82	0.9667
325.75	13.56	0.9661
326.90	14.30	0.9639
327.75	14.92	0.9645
329.35	16.05	0.9615
330.75	17.15	0.9615
331.90	18.08	0.9601
333.25	19.23	0.9592
335.75	21.51	0.9569
338.45	24.25	0.9551
341.00	27.10	0.9535
342.45	28.84	0.9524

by the average value of the relative deviation, which is 0.147%. The regression line was extrapolated to lower values of temperature in order to be compared with experimental results obtained from the literature (the results of [4–7]).

3.3. Water Activity in the K_2SO_4-Saturated Solutions. From the experimental values of the vapor pressure of saturated solutions of K_2SO_4 given in Table 2, the corresponding values of the water activity can be evaluated. In order to perform this calculation, it is proposed that the deviation from the ideal behavior of the vapor pressure can be appropriately described by the virial equation of state, considering only the second virial coefficient $B(T)$. In this case, the logarithm of the water activity can be evaluated from the following expression [13]:

$$\ln a_w = \ln \frac{P_w(T)}{P_w^s(T)} + \frac{(P_w(T) - P_w^s(T))}{RT}[B_w(T) - v_w^o(T)], \tag{2}$$

where $P_w(T)$ is the vapor pressure of saturated solutions of K_2SO_4, values given in Table 2. The values of the vapor pressure of pure water $P_w^s(T)$ were calculated from the equation proposed by Wagner and Pruß [11]. The second virial coefficient for water vapor $B_w(T)$ was evaluated with the equation proposed by Harvey and Lemmon [14]. Finally, the molar volume of liquid water $v_w^o(T)$ was calculated from the relationship between water density and temperature given by Kell [15]. The values of the water activity for the saturated solutions of K_2SO_4 evaluated experimentally are given in Table 2. The correlation of these values leads to the following equation:

$$\ln a_w = -10.2654 - \frac{579.361}{(T/\mathrm{K})} - 1.4607 \ln(T/\mathrm{K}). \tag{3}$$

Figure 3 shows the experimental values (symbols) and the continuous line is the corresponding simulation with (3). It can be observed that this equation describes accurately the water activity of saturated solutions of potassium sulfate in the temperature range 310 K $\leq T \leq$ 345 K. The quality of the water activity correlation can be appreciated by the average value of the relative deviation, which is equal to 0.028%.

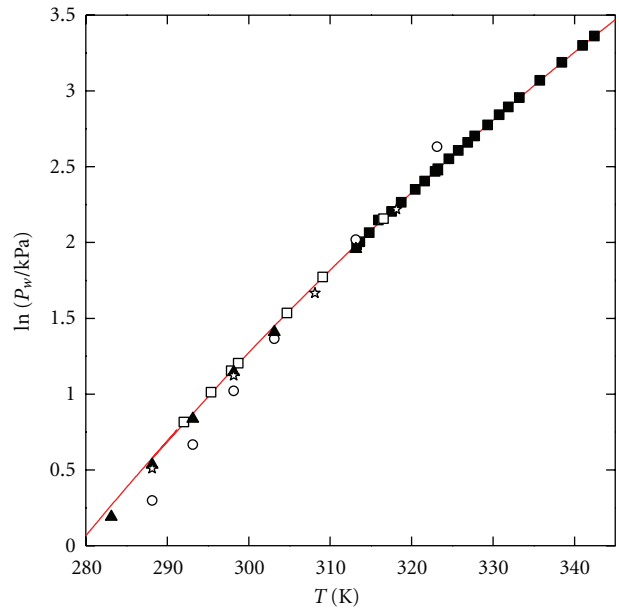

Figure 2: Dependence of the vapor pressure of saturated solutions of potassium sulfate on temperature. (■) experimental; (—) data correlation; (□) [4]; (◯) [5]; (▲) [6]; (☆) [7].

4. Discussion

The experimental evaluation of the vapor pressure of saturated aqueous solutions of potassium sulfate was carried out in the range of temperatures 310 K $\leq T \leq$ 345 K. In this range the solid phase corresponds to the anhydrous salt [16]. From the correlation of the experimental results, the corresponding analytical dependence was derived, which is given by (1). The results obtained were compared with the vapor pressure data reported by Leopold and Johnston [4], Foote et al. [5], and Adams and Merz [6]. There were also included vapor pressure values obtained from dew point measurements evaluated by Wexler and Hasegawa [7]. These data, which correspond to the temperature range 280 K $\leq T \leq$ 323 K, are included in Figure 2. To carry out the comparison, the dependence given in (1), obtained from the correlation of the ours experimental results, was extrapolated up to 280 K. There can be observed in Figure 2 a good agreement between the extrapolation of the correlation (continuous line) and the values of the vapor pressure

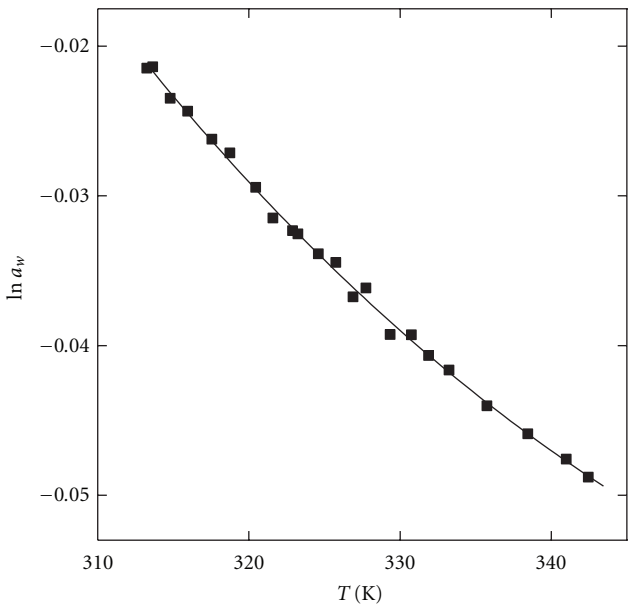

Figure 3: Dependence of water activity of saturated solutions of potassium sulfate on temperature. (■) experimental; (—) data correlation.

obtained from the literature [4–8], except those reported by Foote et al. These results are lower than those of the other authors in the low temperature range, being the corresponding slope of the dependence ln P versus T significantly greater. The origin of this different behavior is unknown but could probably be due to same kind of systematic error in the experimental determination of pressure. Furthermore, when the evaluation of the vapor pressure of the saturated solution at 374.15 K, the unique result shown by Berkeley [8], is carried out by extrapolation with (1), the value P_w = 99.97 kPa is obtained. As the experimental value is P_w = 100.34 kPa, the relative deviation is 0.4%. This result shows an adequate agreement with the scarce data available for the vapor pressure of the saturated solution of potassium sulfate.

5. Conclusions

The experimental evaluation of the vapor pressure of saturated aqueous solutions of potassium sulfate was carried out in the range of temperatures 310 K $\leq T \leq$ 345 K, which was not evaluated previously. The values of the water activity in such solutions were also determined. In both cases, the analytical dependences on temperature were obtained from the correlation of the experimental results, which accurately describe the behavior of these properties in such solution.

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References

[1] A. Apelblat and E. Korin, "The vapour pressures over saturated aqueous solutions of cadmium chloride, cadmium bromide, cadmium iodide, cadmium nitrate, and cadmium sulphate," *Journal of Chemical Thermodynamics*, vol. 39, no. 7, pp. 1065–1070, 2007.

[2] A. Apelblat and E. Korin, "The molar enthalpies of solution and vapour pressures of saturated aqueous solutions of some ammonium salts," *Journal of Chemical Thermodynamics*, vol. 35, no. 5, pp. 699–709, 2003.

[3] A. Apelblat and E. Manzurola, "Solubilities and vapour pressures of saturated aqueous solutions of sodium tetraborate, sodium carbonate, and magnesium sulfate and freezing-temperature lowerings of sodium tetraborate and sodium carbonate solutions," *Journal of Chemical Thermodynamics*, vol. 35, no. 2, pp. 221–238, 2003.

[4] H. G. Leopold and J. Johnston, "The vapor pressure of the saturated aqueous solutions of certain salts," *Journal of the American Chemical Society*, vol. 49, no. 8, pp. 1974–1988, 1927.

[5] H. W. Foote, B. Saxton, and J. K. Dixon, "The vapor pressures of saturated aqueous solutions of certain salts," *Journal of the American Chemical Society*, vol. 54, no. 2, pp. 563–568, 1932.

[6] J. R. Adams and A. R. Merz, "Hygroscopicity of fertilizer materials and mixtures," *Industrial and Engineering Chemistry*, vol. 21, pp. 305–307, 1929.

[7] A. Wexler and S. Hasegawa, "Relative humidity-temperature relationships of some saturated salt solutions in the temperature range 0° to 50°C," *Journal of Research of the National Bureau of Standards*, vol. 53, pp. 19–26, 1954.

[8] E. Berkeley, "On some physical constant of saturated solutions," *Philosophical Transactions of the Royal Society A*, vol. 203, pp. 189–215, 1904.

[9] K. S. Kim, S. Y. Park, S. Choi, and H. Lee, "Vapor pressures of the 1-butyl-3-methylimidazolium bromide + water, 1-butyl-3-methylimidazolium tetrafluoroborate + water, and 1-(2-hydroxyethyl)-3- methylimidazolium tetrafluoroborate + water systems," *Journal of Chemical and Engineering Data*, vol. 49, no. 6, pp. 1550–1553, 2004.

[10] D. R. Lide, *Handbook of Chemistry and Physics*, CRC Press, New York, NY, USA, 2006-2007.

[11] W. Wagner and A. Pruß, "The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use," *Journal of Physical and Chemical Reference Data*, vol. 31, no. 2, pp. 387–535, 2002.

[12] A. Apelblat and E. Korin, "The vapour pressures of saturated aqueous solutions of sodium chloride, sodium bromide, sodium nitrate, sodium nitrite, potassium iodate, and rubidium chloride at temperatures from 227 K to 323 K," *Journal of Chemical Thermodynamics*, vol. 30, no. 1, pp. 59–71, 1998.

[13] J. A. Rard and R. F. Platford, *Activity Coefficients in Electrolyte Solutions*, K. S. Pitzer, CRC Press, Boca Raton, Fla, USA, 1991.

[14] A. H. Harvey and E. W. Lemmon, "Correlation for the second virial coefficient of water," *Journal of Physical and Chemical Reference Data*, vol. 33, no. 1, pp. 369–376, 2004.

[15] G. S. Kell, "Density, thermal expansivity, and compressibility of liquid water from 0° to 155°C: correlations and tables for atmospheric pressure and saturation reviewed and expressed on 1968 temperature scale," *Journal of Chemical and Engineering Data*, vol. 20, no. 1, pp. 97–105, 1975.

[16] A. Seidell and F. W. Linke, *Solubilities of Inorganic and Metallo-Organic Compounds*, vol. 2, American Chemical Society, Washington, DC, USA, 1965.