# Solubilities of Potassium Hydrogen Tartrate and Potassium Chloride in Water + Ethanol Mixtures

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The solubilities of potassium hydrogen tartrate (KHT) in water, water + ethanol, and water + ethanol + KCl, as well as of potassium chloride in water + ethanol mixtures, were determined, using the polythermal method, at different temperatures. Equations were adjusted to the experimental data, enabling the calculation of salts solubilities as a function of temperature and ethanol content in the solvent. For KHT, an additional dependence on the KCl concentration was also included. Experimental data were compared with literature values.

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## Introduction

The potassium salt of tartaric acid, potassium hydrogen tartrate, occurs naturally in wines during the must fermentation. To prevent the unwanted formation of potassium hydrogen tartrate crystals in bottles, most wines are stabilized by crystallization of the salt, prior to bottling.

The modeling of this process makes use of thermodynamic data for potassium hydrogen tartrate in water + ethanol solutions. The activities of potassium hydrogen tartrate can be obtained by an indirect potentiometric method, that requires the presence in the solution of a second salt with a common ion and for which a specific electrode is available.

During the course of this study, solubility data of potassium hydrogen tartrate in water + ethanol mixtures and in the presence of KCl, added as the second salt, were obtained.

The solubility data found in the literature for potassium hydrogen tartrate in water are scarce,[1,2] and there is considerable discrepancy in the results,[1] for temperatures other than 298 K. In other solvents or mixed solvents, potassium hydrogen tartrate solubility data are nonexistent.

For the ternary system KCl + water + ethanol the solubilities available in the older literature[3,4] show deviations from author to author, that, at 25 °C and 20 mass % ethanol, can go up to 3%. Recently published KCl solubility values,[5] obtained over a wide range of ethanol content in the system although at only three temperatures, compare well with some sets of the older data[3] (at 50 °C and 10 mass % ethanol) within ±0.3%.

## Experimental Section

Analytical grade potassium hydrogen tartrate (Merck, 99.5%+) and potassium chloride (Fluka AG, 99.5%+) were used. Prior to measurements, the salts were dried in an oven, at 110 °C, for 24 h. Ethanol was supplied by Pronalab R (99.8%+).

All solutions were prepared using deionized water with the specific conductivity 2 $\mu$S cm$^{-1}$.

***Apparatus and Procedures.*** Solutions were prepared by mass with an uncertainty of $\pm 1 \times 10^{-4}$ g.

The polythermal method developed by Potter and Clynne[6] was used to determine the solubilities presented here.

The experiments were carried out in a tightly sealed 300 mL BOD flask (bottle for the biological oxygen demand determination), equipped with a Teflon-coated magnetic stirrer and immersed in a thermostated bath controlled to ±0.05 K. The temperature was raised by increments which were made progressively smaller as the number and size of the existing crystals decreased (heating rate of about 0.1 K/h near the equilibrium point). Equilibrium conditions corresponding to the bulk composition of the system were assumed to be reached when the last crystal was dissolved.

The temperature was measured in the thermostated fluid with a HP quartz thermometer 2804 A (calibrated to the ITS-90 scale, over the temperature range 273.16 K to 429.7485 K, against the triple point of pure water and the freezing point of indium) and read with a precision of ±0.04 K. The temperature difference outside and inside the BOD flask never exceeded ±0.01 K after 15 min of equilibration. The saturation temperatures reported here are the average values of duplicated measurements with a reproducibility of 0.05 K. To reach temperatures below room temperature, a refrigerator (P Selecta) was used. The saturation temperatures are accurate to ±0.1 K. The uncertainties for the potassium hydrogen tartrate and KCl solubilities are (±0.000 000 6 and ±0.000 01) $\mathrm{kg_{salt}/kg_{water}}$, respectively.

***Solubility Measurements.*** The potassium hydrogen tartrate solubility data were obtained for aqueous solutions containing (0, 0.01, 0.02, and 0.03) m KCl and in aqueous solutions of ethanol (10 mass % in the solvent) containing (0, 0.01, 0.02, and 0.023) m KCl. For all the KCl contents, the potassium hydrogen tartrate solubility data were obtained in the temperature range (277 to 310) K.

The solubilities of KCl in water were obtained from (280 to 360) K. In aqueous solutions of ethanol (5, 10, 15, and 20 mass %, in the solvent), the upper limit of the temperature range explored was progressively reduced, as the ethanol content increased. To prevent evaporation losses of ethanol, the maximum temperature reached for 20% ethanol−water mixtures was 316 K.

## Results and Discussion

***Potassium Hydrogen Tartrate Solubility Data.*** The experimental results for the potassium hydrogen tartrate

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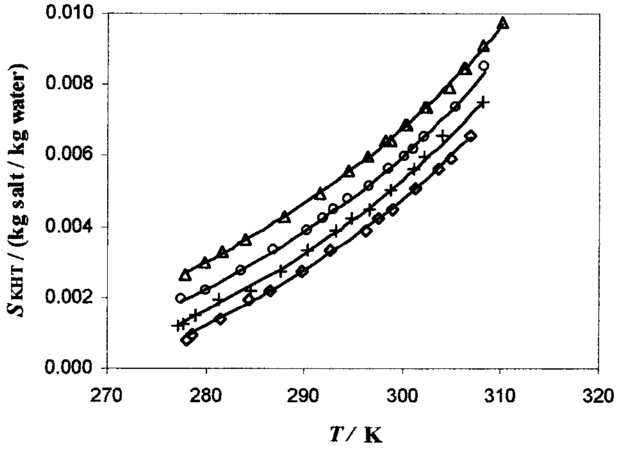

**Figure 1.** Experimental (symbols) and calculated (lines) solubilities of potassium hydrogen tartrate in aqueous solution with different KCl concentrations ($g_{salt}/kg_{water}$): △, 0; ○, 0.75; +, 1.5; ◇, 2.24.

**Table 1. Solubility of Potassium Hydrogen Tartrate, $S_{KHT}$ ($kg_{salt}/kg_{water}$), in Water−Ethanol Mixtures with Various Ethanol Mass Fractions in the Solvent, $w_E$, and for Different KCl Contents, $m_{KCl}$ ($kg_{salt}/kg_{water}$)**

| $T$/K | $10^3S_{KHT}$ | $T$/K | $10^3S_{KHT}$ |
|---|---|---|---|
| $w_E = 0$; $m_{KCl} = 0$ | | | |
| 277.9 | 2.6511 | 300.4 | 6.8682 |
| 280.0 | 2.9771 | 302.3 | 7.3696 |
| 281.8 | 3.2884 | 302.5 | 7.3693 |
| 284.1 | 3.6485 | 304.7 | 7.8994 |
| 288.0 | 4.2969 | 304.8 | 7.9001 |
| 291.7 | 4.9301 | 306.2 | 8.4787 |
| 294.6 | 5.5644 | 306.3 | 8.4789 |
| 296.4 | 5.9697 | 308.1 | 9.1000 |
| 298.2 | 6.4005 | 308.1 | 9.0986 |
| 298.8 | 6.4016 | 310.2 | 9.7593 |
| 300.2 | 6.8625 | | |
| $w_E = 0$; $m_{KCl} = 0.75 \times 10^{-3}$ | | | |
| 277.6 | 1.9511 | 296.6 | 5.1409 |
| 280.1 | 2.1914 | 298.6 | 5.6068 |
| 283.7 | 2.7518 | 300.2 | 5.9483 |
| 286.9 | 3.3190 | 301.1 | 6.1909 |
| 290.4 | 3.8979 | 302.3 | 6.4945 |
| 292.0 | 4.2096 | 305.4 | 7.3827 |
| 293.1 | 4.4944 | 308.4 | 8.4965 |
| 294.5 | 4.7813 | | |
| $w_E = 0$; $m_{KCl} = 1.5 \times 10^{-3}$ | | | |
| 277.3 | 1.2154 | 294.9 | 4.2217 |
| 277.7 | 1.2430 | 296.6 | 4.4596 |
| 279.1 | 1.5018 | 298.8 | 5.0247 |
| 281.4 | 1.9369 | 301.2 | 5.6106 |
| 284.7 | 2.1873 | 302.3 | 5.9454 |
| 287.6 | 2.7491 | 304.1 | 6.5450 |
| 290.4 | 3.3317 | 308.1 | 7.5331 |
| 293.2 | 3.8854 | | |
| $w_E = 0$; $m_{KCl} = 2.2368 \times 10^{-3}$ | | | |
| 278.1 | 0.7961 | 296.3 | 3.8995 |
| 278.6 | 0.9519 | 297.5 | 4.2070 |
| 281.6 | 1.3727 | 299.0 | 4.4853 |
| 284.5 | 1.9413 | 301.4 | 5.0508 |
| 286.6 | 2.1802 | 303.7 | 5.5995 |
| 289.9 | 2.7473 | 305.0 | 5.9229 |
| 292.8 | 3.3159 | 306.9 | 6.5585 |
| $w_E = 0.1$; $m_{KCl} = 0$ | | | |
| 278.2 | 1.2176 | 298.0 | 3.8066 |
| 281.5 | 1.5172 | 301.0 | 4.2998 |
| 285.6 | 1.9077 | 303.2 | 4.7690 |
| 288.9 | 2.3981 | 305.9 | 5.2392 |
| 292.1 | 2.8548 | 308.2 | 5.8054 |
| 294.6 | 3.2903 | 310.7 | 6.3448 |
| 295.7 | 3.4172 | | |
| $w_E = 0.1$; $m_{KCl} = 0.833 \times 10^{-3}$ | | | |
| 279.7 | 0.7646 | 294.9 | 2.5316 |
| 283.4 | 1.0914 | 301.4 | 3.5737 |
| 286.8 | 1.5520 | 307.7 | 4.8577 |
| 292.4 | 2.1694 | 311.9 | 5.9175 |
| $w_E = 0.1$; $m_{KCl} = 1.667 \times 10^{-3}$ | | | |
| 278.8 | 0.2925 | 302.4 | 3.0183 |
| 282.9 | 0.6341 | 305.5 | 3.6542 |
| 287.1 | 1.1173 | 308.5 | 4.2333 |
| 292.0 | 1.5863 | 311.2 | 4.8925 |
| 295.9 | 2.0679 | 313.3 | 5.3984 |
| 299.6 | 2.5560 | | |
| $w_E = 0.1$; $m_{KCl} = 1.944 \times 10^{-3}$ | | | |
| 278.1 | 0.1542 | 301.5 | 2.6915 |
| 282.6 | 0.4831 | 304.6 | 3.1994 |
| 287.0 | 0.9440 | 305.6 | 3.3628 |
| 292.1 | 1.4235 | 308.0 | 3.9505 |
| 295.7 | 1.9435 | 309.4 | 4.3041 |
| 299.4 | 2.3853 | 311.7 | 4.7597 |

solubility, for the different temperatures, ethanol contents, and KCl compositions in the solutions, are reported in Table 1.

To express the solubility of potassium hydrogen tartrate, $S_{KHT}/(kg_{salt}/kg_{water})$, with temperature, $T$/K, and ethanol ($w_E$ = ethanol mass fraction in the solvent) and KCl contents, the following equation was adjusted to the experimental data:

$$S_{KHT} = A_1\left(\frac{\alpha_1 + \beta_1 T}{1 + \chi_1 T}\right)\left(\frac{1 - w_E}{A_1 + w_E}\right) \qquad (1)$$

with $A_1 = \delta_1 + \epsilon_1 w_E T$.

The coefficients $\alpha_1$, $\beta_1$, $\chi_1$, $\delta_1$, and $\epsilon_1$ are KCl concentration dependent, and they can all be described by arbitrary functions of $m_{KCl}/(kg_{salt}/kg_{water})$, $f(m_{KCl})$, of the form

$$f(m_{KCl}) = f_1 + f_2 m_{KCl} \qquad (2)$$

where the $f_i$ are determined by a least-squares fit of eq 1 to the experimental solubility data. The values for the different coefficients are listed in Table 2. The standard deviation of the fit is $6 \times 10^{-5}$ $kg_{salt}/kg_{water}$.

In Figures 1 and 2 the experimental and calculated potassium hydrogen tartrate solubilities, for (0 and 10) mass % ethanol, respectively, are shown.

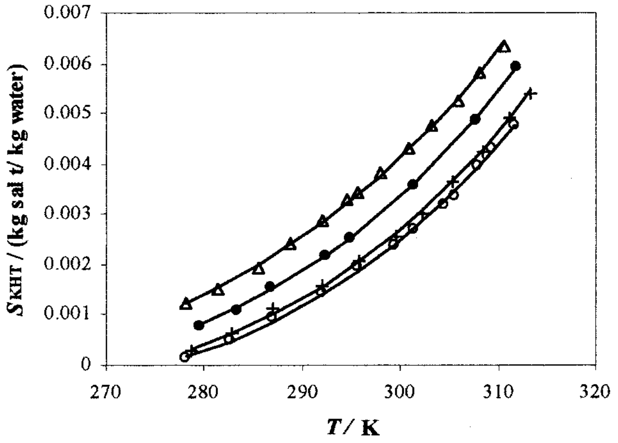

**Figure 2.** Experimental (symbols) and calculated (lines) solubilities of potassium hydrogen tartrate in a 10 mass % ethanol + water mixture with different KCl concentrations ($g_{salt}/kg_{water}$): △, 0; ●, 0.83; +, 1.67; ○, 1.94.

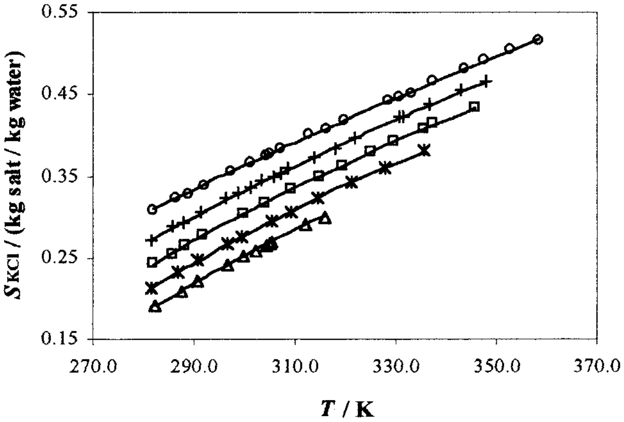

**Figure 3.** Experimental (symbols) and calculated (lines) solubilities of KCl in water + ethanol mixtures, with different ethanol contents (mass %) in the solvent: ○, 0; +, 5; □, 10; ∗, 15; △, 20.

**Table 2. Parameters for Eq 2**

| | $f_1$ | $f_2$ |
|---|---|---|
| $\alpha_1$ | $-5.930\,01 \times 10^{-3}$ | $-1.602\,75$ |
| $\beta_1$ | $2.356\,44 \times 10^{-5}$ | $5.108\,75 \times 10^{-3}$ |
| $\gamma_1$ | $-2.770\,61 \times 10^{-3}$ | $5.505\,92 \times 10^{-2}$ |
| $\delta_1$ | $-1.255\,37$ | $-6.946\,33 \times 10^{-2}$ |
| $\epsilon_1$ | $4.873\,03 \times 10^{-2}$ | $-1.404\,38$ |

**Table 3. Solubility of Potassium Chloride, $S_{KCl}$ ($kg_{salt}$/$kg_{water}$), in Water−Ethanol Mixtures with Various Ethanol Mass Fractions in the Solvent, $w_E$**

| T/K | $S_{KCl}$ | T/K | $S_{KCl}$ |
|---|---|---|---|
| | $w_E = 0$ | | |
| 282.1 | 0.308 58 | 316.2 | 0.407 32 |
| 286.4 | 0.321 98 | 319.9 | 0.417 75 |
| 289.0 | 0.328 05 | 328.6 | 0.442 13 |
| 292.1 | 0.337 88 | 330.6 | 0.446 68 |
| 297.5 | 0.356 04 | 333.1 | 0.451 54 |
| 301.4 | 0.366 35 | 337.3 | 0.464 85 |
| 304.3 | 0.375 30 | 343.8 | 0.480 86 |
| 305.0 | 0.377 62 | 347.5 | 0.490 94 |
| 307.2 | 0.383 04 | 352.8 | 0.505 46 |
| 312.9 | 0.400 08 | 358.3 | 0.515 34 |
| | $w_E = 0.05$ | | |
| 281.8 | 0.271 95 | 308.6 | 0.359 32 |
| 285.9 | 0.288 14 | 313.9 | 0.373 70 |
| 288.1 | 0.292 41 | 318.0 | 0.384 12 |
| 291.4 | 0.306 40 | 322.0 | 0.395 55 |
| 296.3 | 0.322 36 | 330.8 | 0.422 22 |
| 298.7 | 0.329 17 | 331.4 | 0.423 46 |
| 301.4 | 0.336 90 | 336.6 | 0.437 20 |
| 303.3 | 0.343 52 | 343.1 | 0.453 85 |
| 305.7 | 0.348 95 | 347.8 | 0.466 12 |
| 307.1 | 0.352 30 | | |
| | $w_E = 0.10$ | | |
| 282.1 | 0.243 32 | 314.8 | 0.349 62 |
| 285.8 | 0.253 06 | 319.5 | 0.362 38 |
| 288.4 | 0.264 10 | 325.2 | 0.378 67 |
| 291.9 | 0.278 58 | 329.8 | 0.392 77 |
| 299.8 | 0.303 78 | 335.5 | 0.407 37 |
| 304.0 | 0.316 93 | 337.3 | 0.412 78 |
| 309.3 | 0.333 18 | 345.9 | 0.434 20 |
| | $w_E = 0.15$ | | |
| 281.7 | 0.213 01 | 309.2 | 0.305 81 |
| 286.9 | 0.233 11 | 314.7 | 0.323 12 |
| 290.7 | 0.246 87 | 321.2 | 0.341 42 |
| 296.8 | 0.267 52 | 327.8 | 0.360 48 |
| 299.5 | 0.275 35 | 335.5 | 0.380 60 |
| 305.3 | 0.294 56 | | |
| | $w_E = 0.20$ | | |
| 282.2 | 0.190 31 | 304.3 | 0.264 15 |
| 287.5 | 0.208 36 | 305.1 | 0.267 35 |
| 290.9 | 0.222 01 | 305.5 | 0.268 44 |
| 296.5 | 0.240 30 | 312.2 | 0.289 98 |
| 299.9 | 0.250 76 | 315.8 | 0.299 74 |
| 302.2 | 0.258 47 | | |

**Table 4. Coefficients for Eq 3**

| | |
|---|---|
| $\alpha_2$ | $-8.778\ 37 \times 10^{-1}$ |
| $\beta_2$ | $5.378\ 29 \times 10^{-3}$ |
| $\chi_2$ | $-4.147\ 04 \times 10^{-6}$ |
| $\delta_2$ | $1.032\ 20 \times 10^{-5}$ |
| $\epsilon_2$ | $3.924\ 87 \times 10^{-2}$ |

***KCl Solubility Data.*** The experimental results for the KCl solubility, for the different temperatures and ethanol contents, are reported in Table 3.

The experimental solubility data, $S_{KCl}$/($kg_{salt}$/$kg_{water}$), were correlated with temperature, $T$/K, and with the mass fraction of ethanol in the solvent ($w_E$) by the empirical equation

$$S_{KCl} = A_2(\alpha_2 + \beta_2 T + \chi_2 T^2)\left(\frac{1 - w_E}{A_2 + w_E}\right) \qquad (3)$$

with $A_2 = \delta_2 \exp(\epsilon_2 T)$.

$\alpha_2$, $\beta_2$, $\chi_2$, $\delta_2$, and $\epsilon_2$ are empirical constants determined from the least-squares fit to the data. The values are listed in Table 4. Calculated solubilities are in good agreement with the measured values (standard deviation of the fit 0.0017 $kg_{salt}$/$kg_{water}$) as shown in Figure 3.

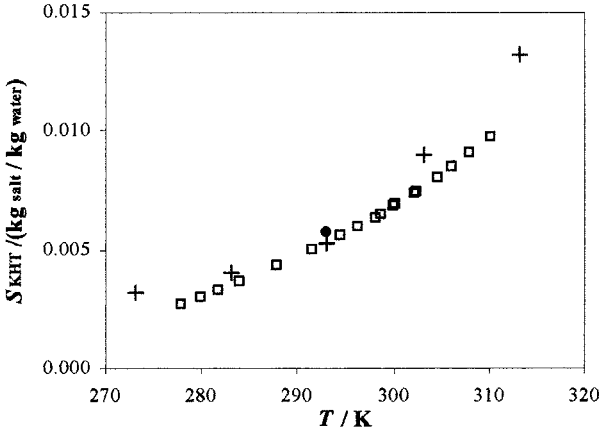

**Figure 4.** Experimental and literature solubilities of potassium hydrogen tartrate in aqueous solution as a function of temperature: □, this work; +, Perry and Green;[1] ●, *Ullmann's Encyclopaedia*.[2]

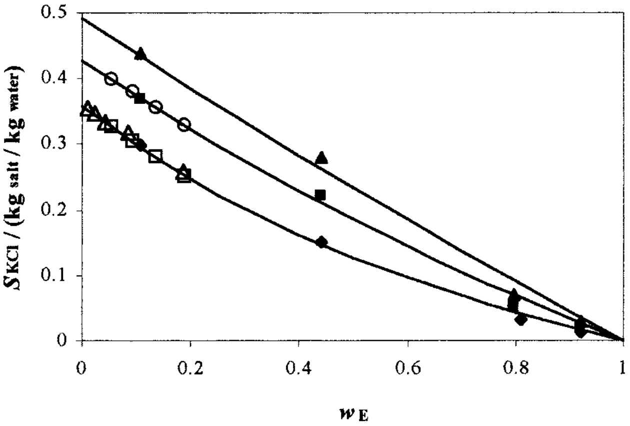

**Figure 5.** Solubilities of KCl as a function of ethanol content in the solvent, for three different temperatures. Lines are calculated values from this work. 298.15 K: □, Gerardin;[3] △, Seidell;[4] ◆, Chiavone and Rasmussen.[5] 323.15 K: ○, Gerardin;[3] ■, Chiavone and Rasmussen.[5] 348.15 K: ▲, Chiavone and Rasmussen.[5]

The experimental solubilities of potassium hydrogen tartrate in aqueous solutions are compared, in Figure 4, with the data available in the literature for this system.[1,2] The agreement between the experimental and literature values is poor, except near room temperature.

Finally, in Figure 5, the experimental solubilities of KCl in water−ethanol are compared with literature values.[4,5] In the temperature range (280 to 360) K and up to 40 mass % ethanol in the solvent, eq 3 represents, within ±5% mass percent salt, most of the literature data.

## Note after ASAP Publication

An incorrect version of Table 2 was used in the original posting of this paper on September 13, 2001. Corrections were made and the paper reposted on September 21, 2001.

## Literature Cited

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