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Effect of potassium chloride on the solvation behavior of caffeine, theophylline and theobromine: Volumetric, viscometric, calorimetry and spectroscopic approach

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ABSTRACT

The density (ρ), speed of sound (u), viscosity (η) and enthalpy of dilution (q) measurements for methylxanthines (caffeine, theophylline and theobromine) in aqueous medium and in aqueous solutions of (0.10–1.00) mol·kg^{-1} KCl covering a temperature range T = (288.15–318.15) K and at p = 101.325 kPa have been accomplished using a density and sound velocity meter, Micro-Ubbelohde type capillary viscometer and Isothermal Titration Calorimetry, respectively. Transfer parameters evaluated from the data suggest that competition among various interactions exists at low and high molalities of $KCl_{(aq.)}$ solutions. The increase in bitterness and decrease in hydration number of methylxanthines with the m_B values have been observed. The dehydration effect of $KCl_{(aq.)}$ at low molalities on the methylxanthines has also been established using ITC. Positive change in the chemical shifts (^{1}H NMR) and increase in absorption intensity (UV–vis) of methylxanthines in the presence of $KCl_{(aq.)}$ further support our results.

1. Introduction

The methylxanthines [caffeine (CAF), theophylline (TPY) and theobromine (TBR)] are present in a variety of foods, beverages and chocolate related products. These are the naturally existing compounds. Therefore, both health professionals and consumers are very much curious to know more about methylxanthines due to their potential physiological effects (Caudle, Gu, & Bell, 2001). Inspite of their food value, they also serve several other roles in our body. CAF may (1) block GABA-A receptors, (2) inhibit phosphodiesterase activity and (3) stimulate Ca^{2+} signaling. TPY is used as bronchodilator drug in chronic obstructive pulmonary disease and for some anti inflammatory effects, etc. TBR is also a weak phosphodiesterase inhibitor and adenosine receptor blocker (Zhong, Tang, Asadzadeh, & Yan, 2017). Interactions of these methylxanthines with the salts have been important both from the biological and food point of view. Salt ions are naturally present in all biological systems (Rodriguez & Romero, 2017) and their interactions with methylxanthines are of significant biological interest, as they affect DNA stability, conformation etc. Intra- and extra-cellular fluids have a significant presence of K^+ and Cl^- ions. Potassium along with sodium are present in blood plasma and extracellular fluids. Ribeiro et al. studied the quaternary diffusion coefficients of CAF using a taylor dispersion method to model the diffusion in pharmaceutical applications (Ribiero, Santos, Lobo, & Esteso, 2010). Cesaro et al. studied thermodynamics of CAF in aqueous denaturant solutions using solubility and partition studies (Cesaro, Russo, & Tessarotto, 1980). Similarly, Santos et al. measured the diffusion coefficients for the aqueous solutions of TPY + KCl system at 298.15 K using taylor dispersion method (Santos, Lobo, Esteso, & Ribeiro, 2011). Methylxanthines may also explicit bitterness flavor and this could be a problem for food and beverage manufacturers. Physico-chemical interactions may change bitterness intensity (Keast, 2008). Aroulmoji et al. elucidated the role of water in taste modalities of CAF and CAF + sucrose mixtures (Aroulmoji, Hutteau, Mathlouthi, & Rutledge, 2001). Salts impart flavor and play a key role by reducing water activity (Barbut, Tanaka, & Maurer, 1986). KCl salt is used as a natural preservative (Breslin & Beauchamp, 1995). KCl has been effective in retarding growth, toxins produced by pathogens and in fermentation also (Bautista-Gallego, Arroyo-Lopez, Duran-Quintana, & Garrido-Fernandez, 2008). KCl is used in many processed foods as thickener, stabilizer and firming agent. Processed food may contain dairy based beverages such as chocolate milk, tea, coffee. KCl is used to replace sodium containing preservatives. So, the taste behavior of methylxanthines in $KCl_{(aq.)}$ solution is interesting to study. To explain the effect of KCl on the methylxanthines, it is vital to study their thermodynamic, transport and spectroscopic properties in aqueous solutions.

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Table 1
Details of the chemicals used.

Chemical Name	Empirical formula	Synonyms	M g·mol^{-1}	Source	CAS number	[a]Solubility in water
Caffeine	$C_8H_{10}N_4O_2$	1,3,7-trimethylxanthine	194.19	Sigma Aldrich	58-08-2	16 mg/ml
Theophylline	$C_7H_8N_4O_2$	1,3-dimethylxanthine	180.16	Sigma Aldrich	58-55-9	8.3 mg/ml
Theobromine	$C_7H_8N_4O_2$	3,7-dimethylxanthine	180.16	Sigma Aldrich	83-67-0	less than 1 mg/ml
Potassium Chloride	KCl		74.55	Sisco Research Laboratories	7447-40-7	more than 100 mg/ml

Where M = molecular weight.
[a] As reported by the suppliers.

The solvation behavior of these drugs in $NaCl_{(aq.)}$ solutions has already been reported in our previous paper (Banipal, Beri, Kaur, & Banipal, 2017). In this paper, we have reported the volumetric, viscometric, calorimetry and spectroscopic properties of methylxanthines in the presence of $KCl_{(aq.)}$ solution.

2. Experimental

Chemical compounds studied in this article: Caffeine (PubChem CID): 2519; Theophylline (PubChem CID): 2153; Theobromine (PubChem CID): 5429; KCl (PubChem CID): 4873.

2.1. Materials

In the present study, all the chemicals used are of high purity grade and their details are mentioned in Table 1. Structures of the solutes have been represented in Scheme 1. The chemicals have been dried in vacuo over anhydrous $CaCl_2$ before use. HPLC analysis of these solutes have been carried out to check the purity and details have been reported elsewhere (Banipal et al., 2017).

2.2. Equipment and procedures

The stock solutions have been made with deionised, double distilled and degassed water having specific conductivity $< 1.3 \times 10^{-4}$ Sm^{-1}. The respective solutions were prepared using a Mettler balance (Model: AB265-S) on mass basis having a precision of ± 0.01 mg. The standard uncertainty in molality comes out to be ± 2.8·10^{-4} mol·kg^{-1}.

2.2.1. Density and speed of sound

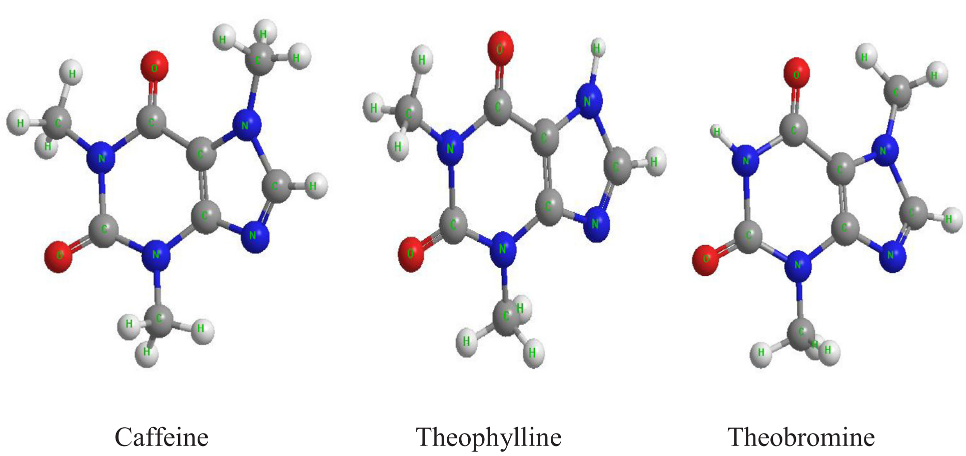
The density (ρ) and speed of sound (u) measurements were performed with the help of vibrating-tube digital density and sound velocity meter (DSA 5000M, Anton Paar). The two-in-one instrument is equipped with both density and sound velocity cells. The temperature of both the cells is maintained by a built-in Peltier thermostat (PT-100) within ± 0.001 K. The calibration procedure was performed at 293.15 K with triple distilled, degassed water, and with dry air at atmospheric pressure. The accuracy of the instrument in density and speed of sound measurements are of 1×10^{-3} kg·m^{-3} and 0.1 m·s^{-1}, respectively. Standard uncertainty of the density is 0.01 kg·m^{-3} (by taking 1% uncertainity in density due to impurity in samples).

2.2.2. Viscosity

A suspended level Micro-Ubbelohde capillary viscometer has been used for the measurement of solution viscosities, η. The working of the instrument has been reported in our previous paper (Banipal et al., 2017). The standard uncertainty in viscosity, u (η) on an average basis is ± 0.012 mPa·s (considering 1% uncertainty in the viscosity of calibrated water). The correct working of viscometer has been checked by measuring the viscosities of glycine $_{(aq.)}$ solutions at T = 298.15 K which match very well with the literature values (Zhao, 2006). Viscosities of pure water have been taken from the literature (Kestin, Sokolov, & Wakeham, 1978). The conversion of molalities into molarities has been accomplished with the help of density data.

2.2.3. Isothermal titration calorimetry (ITC)

The enthalpies of dilution, q have been measured using an Isothermal Titration Calorimeter (MicroCal iTC200, USA) having a temperature stability within ± 0.005 K. The titrations have been carried out using an automated instrument controlled syringe having volume capacity of 40 µL and stirring at 500 rpm, into the sample cell containing 200 µL of the respective solvent. Total 19 consecutive injections (2 µL each) with duration of 120 s time interval have been performed for each titration experiment. Control experiments of blank water-water experiment and dilution of KCl were performed and corrections have been applied to the main experiment. The titration data were analyzed using Microcal Origin (version 7.0). The calorimeter has been calibrated by performing a complexation reaction between $CaCl_2$ and EDTA solution in MES buffer (pH = 5.6) (Banipal, Kaur, & Banipal, 2016).



Scheme 1. Structure of methylxanthines.