

Thermodynamic study of quercetin and rutin mixtures with alcohols

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ABSTRACT

The paper presents interactions between quercetin (3,3',4',5,7-pentahydroxyflavone) and its glycoside, rutin with short chain alcohols, methanol, ethanol and 1-propanol studied by the surface tension measurements. An attempt was made to investigate the effect of flavonoid and alcohol concentrations as well as temperature on the thermodynamic parameters of alcohols adsorption at the water-air interface that is the standard free enthalpy, enthalpy and entropy of adsorption as well as the infinite dilution activity coefficient. The obtained results show that the mixtures of quercetin with methanol and rutin with ethanol are characterized by the best adsorption properties but all studied systems become less structured after adsorption.

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1. Introduction

Flavonoids are a large subclass of natural polyphenols widely distributed in plants. They are accumulated in almost all plant organs. Some are responsible for colours of fruit (mainly in the skin), veins of leaves, petals of flowers [1,2]. Numerous flavonoids were extensively studied for their various biological activities and beneficial effects on human health. Flavonoids such as quercetin (3,3',4',5,7-pentahydroxyflavone) and its glycoside, rutin are potent antioxidants [3]. Quercetin was often chosen as an active main because it is considered the most powerful antioxidant, and the most widely distributed in nature [4]. Moreover, it has already been used for its anti-inflammatory and anti-tumour activities as well as for cellular protective properties in brain, liver, kidney and colon diseases [5–7].

However, in spite of exhibiting a wide range of pharmacological properties, quercetin and other flavonoids present two obstacles for their pharmaceutical use. The first problem is poor solubility in aqueous media [8] and the second is the sensitivity of flavonoids to oxidative degradation, resulting in poor stability in the aqueous aerobic environment [9]. Lauro et al. found the quercetin solubility at room temperature to be $c_q = 7.7$ mg/L [10]. The poor solubility can be increased by organic solvents [11,12], ionic liquids [13], supercritical water [14] or supercritical carbon dioxide in combination with ethanol [15]. Ethanol is one of the best solvents for quercetin however, the stability of quercetin in ethanol and in water at higher temperatures is limited [16,17]. For rutin isolation the

methanol, methanol/water and buffered methanol/water mixtures are the most frequently employed extractants [18]. However, to determine proper solvents and to design an optimized production process, the interactions between a given flavonoid and solvent at the bulk phase and at different interfaces should be known. The solvents affect greatly the molecular properties such as bond length, polarizability, electron distribution, dipole moments, relative stabilities of different conformers and spectroscopic parameters.

The short chain alcohols, that is methanol, ethanol and propanol, used not only as solvents, but also co-solvents or co-surfactants have always been considered as interesting due to their anomalous behaviour which depends mainly on the solution microstructure [19–24]. This microstructure of the bulk phase of aqueous solutions of alcohols is governed by the hydrogen bonds, hydrophobic interactions and hydration which are reflected in the enthalpy and entropy contributions to the free enthalpy of solutions [24,25]. In the literature it can be found that alcohol self-association takes place in the aqueous solution and that the structure of aqueous solutions of short chain alcohols is characterized by individual alcohol aggregates and water clusters without a significant amount of alcohol–water mixed aggregates [26,27] or in contrast that ethanol and 1-propanol form strong hydrogen bonds with water and exist as inhibitors in clathrate hydrate formation [28]. Independently of the opinions about the structure of the aqueous solutions of short chain alcohols, it is known that their structure would influence the intramolecular or intermolecular interactions with different molecules [29,30], including flavonoids thereby the anti-oxidative effects of the flavonoids molecule. Thus the purpose of the presented studies was to determine the

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thermodynamic parameters of adsorption at the water-air interface that is the standard Gibbs free energy (ΔG_{ads}^0), enthalpy (ΔH_{ads}^0) and entropy (ΔS_{ads}^0) of adsorption as well as the infinite dilution activity coefficient (γ_{ads}^∞) of water-alcohol solutions of quercetin and rutin. For this purpose the surface tension of water-methanol (MeOH), water-ethanol (EtOH) and water-1-propanol (PrOH) solutions of quercetin and rutin ($C = 4 \times 10^{-5}$ and 10^{-4} M) in the wide range of alcohol concentration ($C_p = 0$ –80%) was measured at $T = 293$, 303 and 313 K.

2. Experimental

Quercetin (Q) (Sigma-Aldrich), rutin (Ru) (Sigma-Aldrich), methanol (MeOH) (PoCh), ethanol (EtOH) (PoCh) and 1-propanol (PrOH) (PoCh) were used without further purification. The aqueous solutions of quercetin and rutin with alcohols were prepared using doubly distilled and deionized water (Destamat Bi18E). The surface tension of water was always checked before the solution preparation.

The equilibrium surface tension of water-alcohol solutions of quercetin and rutin was measured at 293, 303 and 313 K by a Krüss K9 tensiometer according to the platinum ring tensiometer method (du Nouy's method). The measured surface tension values were corrected according to the procedure of Harkins and Jordan [31]. The ring was cleaned with distilled water and heated to red colour with a Bunsen burner before each measurement. In all cases more than 10 successive measurements were made. The standard deviation depending on the surfactant concentration range was from ± 0.1 to ± 0.2 mN/m. The temperature was controlled by a jacketed vessel joined to the thermostatic water bath with the accuracy ± 0.01 K.

3. Results and discussion

The measured values of the surface tension (γ_{LV}) of water-alcohol solutions of quercetin and rutin at the different temperatures are presented in Figs. 1–6 together with the literature data values of surface tension of water-alcohol solutions (γ_{LV}^a) at 293 K [24] (Figs. 1, 3 and 5) for comparison. From these figures it results that the surface tension of the studied alcohol-quercetin/rutin solutions decreases with the alcohol concentration which extends with the length of the hydrocarbon chain of alcohol. This reduction of

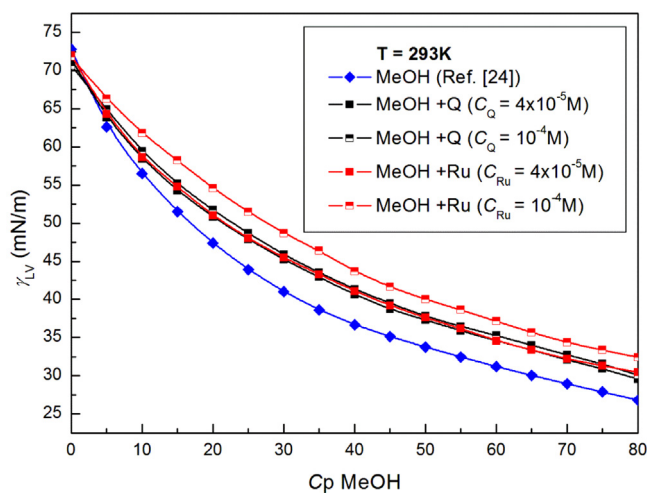


Fig. 1. The values of the surface tension, γ_{LV} , of the aqueous solutions of MeOH [24] as well as the aqueous solutions of MeOH with different concentrations of quercetin and rutin ($C = 4 \times 10^{-5}$ and 10^{-4} M) at $T = 293$ K vs. C_p of MeOH.

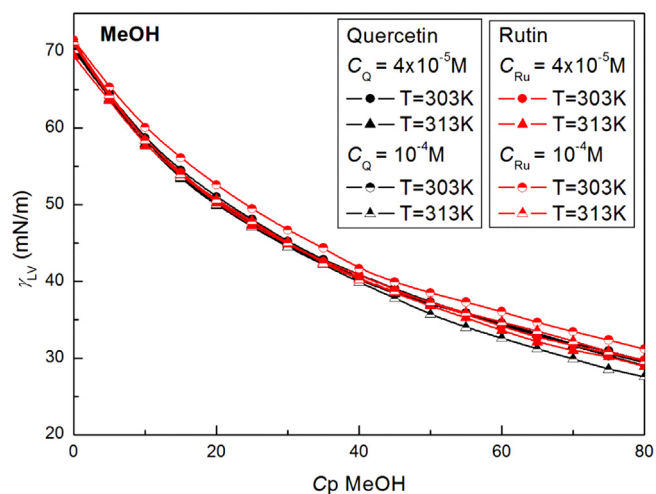


Fig. 2. The values of the surface tension, γ_{LV} , of the aqueous solutions of MeOH with different concentrations of quercetin and rutin ($C = 4 \times 10^{-5}$ and 10^{-4} M) and $T = 303$ and 313 K vs. C_p of MeOH.

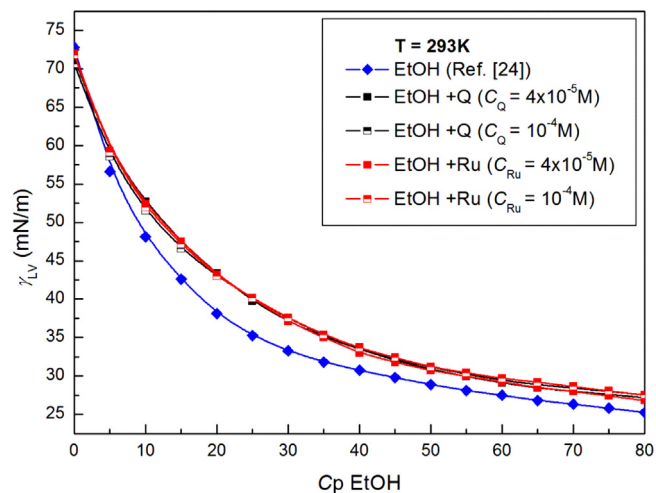


Fig. 3. The values of the surface tension, γ_{LV} , of the aqueous solutions of EtOH [24] as well as the aqueous solutions of EtOH with different concentrations of quercetin and rutin ($C = 4 \times 10^{-5}$ and 10^{-4} M) at $T = 293$ K vs. C_p of EtOH.

surface tension of water-flavonoid solutions is predominantly related to the water-water H-bonds reduction, which is caused by the presence of alcohol molecules [19,23] and for the mixtures of ethanol and 1-propanol with flavonoids it is the largest in the low concentration range, $< 20\%$ which is consistent with the changes of the surface energy values calculated by Phan et al. [23]. From the comparison of the literature data of the surface tension of water-alcohol mixtures at $T = 293$ K (γ_{LV}^a) [24] with those with quercetin and rutin at different concentrations (Figs. 1, 3 and 5) it results that the latter are higher than the first ones. Also if these values are compared for $C_p = 40\%$, it results that the addition of quercetin and rutin has the slightest influence on the values of γ_{LV} of PrOH solutions that is the difference between γ_{LV}^a and γ_{LV} is equal to 0.51 ($C_Q = 4 \times 10^{-5}$ M), 0.98 ($C_Q = 10^{-4}$ M), 0.31 ($C_{Ru} = 4 \times 10^{-5}$ M) and 0.76 ($C_Q = 10^{-4}$ M), in contrast to methanol where the values of $\gamma_{LV}^a - \gamma_{LV}$ are the greatest and equal to 3.96, 4.68, 4.43 and 7.00 mN/m, respectively. To explain this fact taking into account the measured values of γ_{LV} the standard free enthalpy of adsorption of a given alcohol in flavonoid solutions at the water-air interface (ΔG_{ads}^0), that is the measure of the

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