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# HYDROPHOBIC EFFECTS IN WATER AND WATER/UREA SOLUTIONS

#### A COMPARISON

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#### ABSTRACT

The partition of several n-alkanols, from methanol to n-nonanol, between n-hexane and water and between n-hexane and water containing 20 % (w/v) urea has been measured at temperantures ranging from 0 °C to 60 °C. The standard free energy of transfer from water to the urea containing solution decreases with the length of the alkyl chain, being positive for the small alcohols and negative for the higher alkanols. The same tendency is observed upon all the temperature range considered. On the other hand, the standard entropy of transfer from water to the urea containing solution increases with the length of the alkyl chain of the alkanol. These results are compatible with a simple description of the urea effect in terms of increasing the entropy of dissolution of the hydrophobic alkyl chain in the aqueous solution.

#### RESUMO

As constantes de partição de álcoois variando de metanol a n-nonanol foram medidas para água e n-hexano e n-hexano e água contendo 20% (peso/volume) de uréia a temperaturas entre 0 °C e 60 °C. A energia livre padrão de transferência de água para solução contendo uréia diminui em função do comprimento da cadeia alquila, sendo positiva para álcoois curtos e negativa para álcoois de cadeia comprida. Por outro lado, a entropia padrão de transferência de água para a solução contendo uréia aumenta em função do comprimento da cadeia do álcool. Os resultados experimentais são compatíveis com a simples descrição do efeito da uréia em termos do aumento da entropia de dissolução da cadeia alquila na solução aquosa.

#### INTRODUCTION

The properties of aqueous solutions of urea are interesting and intriguing. The solubility of urea in water is extremely high ( > than 20 M at room temperature <sup>1</sup>) and solubilization takes place following almost ideal behaviour.<sup>2</sup> Addition of urea to water increases the solubility of nonpolar solutes with relatively large size but decreases (or barely affect) the solubility of the small size members of this type of solutes at room temperature ; the size discriminating effect of urea on solubility of nonpolar solutes is more important at low temperatues.<sup>3</sup> Urea in aqueous solution is a strong protein denaturant<sup>4</sup>, it inhibits the micellization of surfactants and alter micellar characteristics 5-15. All these properties of aqueous urea solutions have been the subject of numerous studies performed with the aim to clarify the mechanism of urea action. From these studies, two plausible mechanisms have been proposed  $^{3,16}$ : (1) An indirect mechanism in which urea acts only at the level of the solvent, altering the structure of water in a way that facilitates the dissolution of hydrophobic species (i.e., by invoking the capacity of urea to act as a "water structure breaker", so allowing the free energy required for cavity formation to decrease) and, (2) A direct mechanism in which urea participates in the solvation of hydrophobic species by replacing some water molecules in the hydration shell of the solute. Mechanism (1) has received the majority of the attention in the literature, an many experimental studies seem to support it. 17,18 However, recent experiments seem to contradict it.<sup>19</sup> Furthermore, computersimulation studies indicate that urea hardly affects the structure of water, going against mechanism (1) and that a few molecules of water around a hydrophobic moiety are replaced by urea, consistent with mechanism (2).<sup>20</sup> In recent years, mechanism (2) is increasingly employed and several studies seem to support the hypothesis of a direct mechanism of urea action. 10,11,14

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Due to the potential applicability of either mechanism of urea action, the literature data on the effects of urea in micellar solutions are conflicting. Miyagishi et al.<sup>7</sup> performed an study on the alterations in properties of micelles induced by perturbation in the external environment and used urea as an additive assumed to be able to penetrate the micelles. Similarly, urea was assumed to be a nonpenetrating agent in a study performed by Gonzalez at al.<sup>6</sup> on the effect of additives upon the solubility of naphthalene derivatives in micellar solutions. Alternatively, recent studies are in line with the participation of a direct mechanism of urea action in several properties of micelles. <sup>10,11,14,15</sup> Furthermore, the effect of urea upon the critical micelle concentration of surfactants seems to be non understable in terms of either mechanism of urea action upon the solubility of the hydrocarbon parts of the amphiphiles / strong effects of the surfactant head groups must be exerted and / or, more likely, the effect of urea upon the cmc of surfactants a change in the chemical potential of the surfactant in the also reflects micelle. If this were the case, the question arises on whether urea replaces water at the micelle surface (mechanism (2) or the alterations of the chemical potential of the surfactant in the micelle are simply due to a facilitated solvation of the first methylene groups near the head groups (mechanism 1). As an example, urea barely modifies the critical micelle concentration (cmc) of sodium dodecylsulphate,<sup>5,8</sup> while it considerably increases the cmc of dodecyltrimethylammonium bromide<sup>8,12</sup> and cetyltrimethylammonium bromide.<sup>6</sup> Ideally, studies on the thermodynamics (free energy, entropy and enthalphy) of transference of surfactants from water to urea solutions performed at surfactant concentrations well below the critical micelle concentration in water would help to clarify some of these aspects. Unfortunately, these type of studies are scarce.<sup>21</sup>

Primary alkanols afford an homologous series of amphiphilic molecules with identical

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head groups in which the size of hydrophobic moiety can be widely varied by simply changing the hydrocarbon length, its concentration in dilute solutions is easy to measure and have been employed in several studies on hydrophobic interactions. <sup>22</sup> We have selected this series of compounds to perform an study on the thermodynamic parameters involved in the transference of methylene groups from water to aqueous urea solutions. The results are here reported.

#### **MATERIALS AND METHODS**

The partition of the alkanols between water and n-hexane was evaluated by the shake flask method. The alkanol was dissolved in water (or water containing 20 % w/v urea) at concentrations far below saturation and, after addition of n-hexane, the flasks were shaken by several minutes at the desired temperature. The solutions were kept two hours in closed tubes in a thermostatized bath and samples from both phases were analyzed by gas chromatography. The alkanols were Aldrich products of the highest purity available and were employed without purification. Since the concentration of the alkanol in both phases was evaluated chromatograph ically after equilibration, the posible presence of impurities does not interfere with the results.

#### **RESULTS AND DISCUSSION**

At the low alkanol concentrations employed in the present work, the thermodynamic partition constant can be directly obtained from the ratio of the concentrations in the organic and aqueous phase:

$$K = [ROH]_{hex} / [ROH]_{water}$$
(1)

The values obtained at 0, 25 and 40 °C when water or water plus urea were employed as aqueous phase, are compilled in Table 1. These data allow an evaluation of the free energy change associated to the transfer of the alkanol from water to water/urea solutions ( $\Delta(\Delta G^{\circ})$ ). The values obtained at 0 °C and 25 °C are shown in Fig. 1. Although they are rather small and affected by high relative errors, they indicate that the transfer becomes more favoured when the length of the alkyl chain increases. The same tendency is observed for the data at 40 °C previously reported by Abu- Hamdiyyah et al. <sup>9</sup>, which have also been included in Fig. 1. These results imply that addition of urea to water decreases the magnitude of the hydrophobic effect. Similar conclusions can be derived from the data obtained at the other temperatures, which show that the effect of the alkyl chain length upon  $\Delta G^{\circ}$  becomes larger at lower temperatures.

Alkanol	0 °C		25 ℃		60 °C	
	water	water/urea	water	water/urea	water	water/urea
Methanol	0.0012	0.0035	0.0029	0.0046	0.0052	0.0081
Ethanol	0.0020	0.0030	0.0053	0.0070	0.0160	0.0250
Propanol	0.0110	0.0150	0.025	0.032	0.1	0.1
Hexanol	0.98	1.13	3.35	2.45	9.5	6.4
Octanol	21.6	19	67.1	59	155	83
Nonanol	76	20	145	100	345	240

 Table 1.
 Partition Constants at different temperatures



Carbon number

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Figure 1.

values of the standard free energies of transfer (in cal/mol) from water to water/urea solutions plotted as a function of the number of carbon atoms in the alkanols. (△) Data obtained at 0 °C; (○) Data obtained at 25 °C; (□) Data obtained at 40 °C; (□) Data reported at 40 °C in Ref. 9.

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The changes in enthalpy and entropy associated to the transfer processes can be obtained from the change with temperature of the ln K. Typical values obtained are given in Fig. 2. The curvature of the plot indicate that the enthalpy changes,  $\Delta H^{\circ}$ , cannot be considered as constant and makes difficult the calculation of the values of the thermodynamic quantities. In order to obtain an estimation of them, the data were fitted to a parabola and the slope at 25 °C analytically derived. The values obtained for the transfer from n-hexane to aqueous solutions are shown in Fig. 3. From these values and the free energy changes, the entropy changes  $\Delta S^{\circ}$ can be derived. The values obtained are shown in Fig. 3. Although these values are affected by rather large uncertainties, they show that passage from the organic solvent to the aqueous phase implies a significant decrease in both, enthalpy and entropy. In particular, it is noticeable the steady increase in  $\Delta S^{\circ}$  with the size of the alkyl chain. Similar trends are observed when the transfer from the organic solvent to the urea/water solution is considered. The effect of urea can be best analyzed by considering the transfer from the aqueous solution to the urea/water solution. The values of  $\Delta H^{\circ}$  and  $T\Delta S^{\circ}$  associated to the transfer of the alkanols from water to urea/water solutions are given in Fig. 4. The data given in this figure show compensatory effects in  $\Delta H^{\circ}$  and  $T\Delta S^{\circ}$  which can be partly due to the rather large experimental errors involved in their determination. However, the results indicate that, particularly for the larger alkyl chains where the hydrophobic effect must be maximal, the transfer from water to urea/water solutions take place with both an increase in  $\Delta H^{\circ}$  and  $T\Delta S^{\circ}$ , a result compatible with a reduced hydrophobic effect in the presence of urea. This is fully compatible with the data of Fig. 1 which indicate that transfer of the alkanol to the urea/water solution becomes more favoured when the length of the



Figure 2. Dependence of the n-hexane/water (O) and n-hexane/water plus urea ( $\Delta$ ) partition constants with temperature. Data plotted as R ln K (in cal/mol) against the inverse of the temperature (Kelvin)

- (A) Data obtained for methanol
- (B) Data obtained for 1-nonanol.

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Figure 3. Dependence of the enthalpy and standard entropy of transfer (in kcal/mol) from n-hexane to water with the number of carbon atoms of the alkanol. Values reported were obtained at 25 °C.



Figure 4. Dependence of the standard enthalpy and standard entropy changes for the transference from water to water/urea solutions with the number of carbon atoms of the alkanol. Values reported were evaluated at 25 °C.

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alkyl chain increases. Although these results do not allow to establish the origin of these effects (either reducing the structure of water and/or a direct interaction of urea with the alkyl chain), they clearly indicate that the decreased free energy of the alkyl chain in the urea/water solutions, relative to that in aqueous solution, is mostly due to a larger partial entropy of the solute in the presence of the additive.

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