The Solubility of Gaseous Hydrocarbons and the Hydrophobic Effect in Aqueous Solutions of Alkylureas

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The solubility of methane and ethane in aqueous solutions of some alkylderivatives of urea have been studied in order to evaluate the hydrophobic effect according to the Ben-Naim model [1]. The cosolutes used are monomethylurea (MMU), monoethylurea (MEU), symmetric dimethylurea (1,3-DMU) and symmetric diethylurea (1,3-DEU). The study is of potential interest for its biochemical and biophysical implications [1, 2]. In fact, hydrocarbons can be considered as model molecules of some of the side chains of proteins and, at the same time, it is known the capability of alkylureas in denaturing globular proteins [3–5].

The standard free energies of solution for the gases are deduced from the Ostwald absorption coefficient γ_s:

$$\Delta\mu^\circ_s = -RT \ln \gamma_s$$

From the temperature derivatives of the free energies, the standard enthalpies and entropies of solubilization are also obtained. It is already known that the last two quantities are negative for the apolar gases in water, and we found that the addition of the studied series of cosolutes do not introduce drastic variations in this behaviour. The signs of the enthalpy and entropy were ascribed [6] to an enhancement of water structure, promoted by the apolar gases.

A quantitative scale of comparison for the intensities of the hydrophobic interactions was proposed by Ben-Naim and coworkers [1]. The mechano-statistical treatment leads, with certain assumptions, to the simple relation:

$$\delta G^{\mathrm{HI}}(R_1) = \Delta\mu^\circ_{\mathrm{Et}} - 2\Delta\mu^\circ_{\mathrm{Me}}$$

where $\Delta\mu^\circ_{\mathrm{Et}}$ and $\Delta\mu^\circ_{\mathrm{Me}}$ are the free energies associated with the process of transfer, at constant P and T, of two molecules of methane from fixed positions at infinite distance to a defined distance R_1 in the presence of the solvent respect to the vacuum.

The changes of δG^{HI} with the concentration of the cosolutes (alkylureas) and with the temperature, hence the signs and values of the corresponding δH^{HI} and δS^{HI}, are analyzed and compared with the free energies of transfer $\Delta\mu^\circ_{\mathrm{tr}}$. Qualitative conclusions are tried on the mechanisms ruling the complex phenomenon of the solubilization of gaseous hydrocarbons in aqueous mixed solvents and on the self and cross interactions among the different species in solution.

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Solute–Solvent Interactions in Water–Sulfolane Mixtures

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We have studied the conductometric and calorimetric behaviour of some ions in water–sulfolane mixtures (H_2O–TMS).

The conductometric results [1] have been analyzed by considering the dependent on the solvent composition of the ionic Walden products in the mixtures relative to the corresponding values in pure water [$R = (\lambda^\pm_o\eta_o)_s/(\lambda^\pm_o\eta_o)_w$]. $R < 1$ values for the ions Br^-, I^- and ClO_4^- and the order $R(Cl^-) > R(Br^-) > R(I^-) > R(ClO_4^-)$ observed in water-rich mixtures may be explained on the basis of the decrease in the structure-breaking capacities of these ions as a result of the decrease in the degree of structure of water caused by TMS. In the case of Na^+ and K^+ ions, $R > 1$ values seem to be scarcely affected by structural phenomena and may be explained by assuming that the interactions between the ions and the solvents in the mixtures are mainly of the acid–base type (sorting effect) [2].

The structure decrease of water caused by TMS determines ion transfer enthalpies $\Delta\Delta H^\circ_s$ from H_2O to H_2O–TMS mixtures negative for the ions Na^+, K^+, I^- and ClO_4^-. The ions Cl^- and Br^- show positive, increasing $\Delta\Delta H^\circ_s$, with a more marked increase over 60 mole% TMS. This behaviour is mainly determined by the decrease of hydrogen-bonding interactions between these ions and water, caused by addition of TMS, particularly in TMS-rich mixtures [3].

The capacity of TMS to break water structure in small percentages too has been also shown by the regular decrease of partial molal heat capacities of Bu_4NBr and Am_4NBr which we have observed in the range 0–20 mole% TMS [4].

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The Effect of Axial Dispersion on Mass Transfer between Gases and Liquids in Trickle Bed Reactors

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The cocurrent flow of gas and liquid through a packed bed is an extensively used operation in chemical industries where mass transfer and fluid dynamics affect the design equations. Reported overall mass transfer coefficients between gases and liquids are considered usually with the assumptions of plug flow for both phase [1]. That may be valid for gas phase, however liquid backmixing, where axially dispersed plug flow model is an adequate representation, are expected especially for short trickle bed reactors [2]. The effect of axial dispersion on mass transfer coefficients should be minimized and the true overall mass transfer coefficients should be used for design purposes.

According to the model transient mass conservation equations for gas and liquid phases are

$$\frac{\epsilon G\partial C_G}{\partial t} = -u_G\frac{\partial C_G}{\partial z} - K_La(HC_G - C_L) \qquad (1)$$

$$\frac{\epsilon L\partial C_L}{\partial t} = -u_L\frac{\partial C_L}{\partial z} + K_La(HC_G - C_L) + + D_L\frac{\partial^2 C_L}{\partial z^2} \qquad (2)$$

where C is concentration, u is superficial velocity, K_La is overall gas liquid mass transfer coefficient, D_L is axial dispersion coefficient, ϵ is hold up volume fraction, H is reciprocal of Henry's law constant. The subscripts G and L stands for gas and liquid respectively. Initial and boundary conditions can be stated as; at $t = 0$, $C_G = C_L = O$ for all z; at $z = 0$, $C_G = M\delta(t)$, and $-D_L\partial C_L/\partial z + u_LC_L = 0$; at $z = Z$, $\partial C_L/\partial z = 0$ at any time t.

Simultaneous solution of equations *1* and *2* with boundary conditions resulted the following expression for m^*_{OL} that is the fraction of species transferred to liquid phase in infinite time at column height z.

$$m^*_{OL} = (u_LH/u_LH + u_G)\,(1 - e^{BZ}/A)$$

where

$$A = 0.5(1 + e^{-bZ}) +$$

$$+ (1 - e^{-bZ})(K_La(u_LH + 2u_G)/u_Gu_L2 - u_L/2D_L)/b,$$

$$B = 0.5\,(u_L/D_L - K_LaH/u_G - b)$$

$$b = ((K_LaH/u_G + u_L/D_L)^2 + 4K_La/D_L)^{0.5}$$

When axial dispersion is neglected, $A = 1$ and B is a function of K_La only [3]. The model may consider adsorption by including a similar mass conservation equation written for the species in the pores of catalyst particals and mass transfer term from liquid to solid in eqn. (*2*).

Experimental studies are done with nitrogen flowing cocurrently with water at 20 °C and 1 atmosphere in a laboratory size trickle bed reactor packed with active carbon pellets. Impulse of sulfur dioxide is given to gas phase.

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A Thermodynamic Study on Hydrolytic Reactions of Divalent Metal Ions in Aqueous and Dioxane–Water Mixed Solvents

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We have studied hydrolytic reactions of various divalent metal ions such as beryllium, copper, nickel,