mined 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

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

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

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, cadmium and lead in aqueous and dioxane–water mixed solvents containing 3 mol dm^{-3} $LiClO_4$ as a constant ionic medium at 25 °C [1–4].

It has generally been found that the composition of the hydrolytic species and the formation constant $^*\beta_{pq}$ for the reaction $qM^{z+} + pH_2O = M_q(OH)_p^{(qz-p)+} + pH^+$ were little affected by the solvent composition up to 0.5 mole fraction (*ca.* 88% w/w) of dioxane in the medium. Free energy changes of transfer, $\Delta G^t_{pq} = -RT[\ln\{\beta_{pq}(mix)/\beta_{pq}(aq)\}]$ for the reaction: $qM^{z+} + pOH^- = M_q(OH)_p^{(qz-p)+}$ ($\beta_{pq} = [M_q(OH)_p^{(qz-p)+}]/[M^+]^q[OH^-]^p = {}^*\beta_{pq}/K_i^p$; K_i denotes the autoprotolysis constant of the solvent) were strongly dependent on the composition and charges of the complexes. However, the values $(1/p)\Delta G^t_{pq}$ were approximately independent of the complexes examined at a given concentration of dioxane. Since the free energy change of transfer can be expressed as $(1/p)\Delta G^t_{pq} = (q/p)((1/q)\Delta g_{pq} - \Delta g_M) - \Delta g_{OH}$ (Δg_i stands for the partial molar free energy change of transfer of species i) and the contribution of Δg_{OH} to $(1/p)\Delta G^t_{pq}$ is the same in all the cases, the results obtained indicated that the values, $(1/q)\Delta g_{pq} - \Delta g_{M'}$ depend only on p/q (= $z - z'$ where z' represents the formal charge per metal ion of the complex).

Enthalpy changes for the hydrolytic reactions of some divalent metal ions and the autoprotolysis reaction of the solvents were determined by use of a fully automatic on-line-controlled system developed in our laboratory [5] and the enthalpy and entropy changes of transfer of the reaction, ΔH^t_{pq} and ΔS^t_{pq}, respectively, were evaluated. The value, $(1/p)\Delta H^t_{pq} = (q/p)((1/p)\Delta h_{pq} - \Delta h_M) - \Delta h_{OH}$, strongly depended on metals, where Δh_i denotes the partial molar enthalpy change of transfer of species i. For a given metal ion, $(1/p)\Delta H^t_{pq}$ became more negative (or less positive) with an increase in z' in the complex, and at a given z' the value was practically independent of the composition of the complexes. The results obtained indicated that the value of $(1/q)\Delta h_{pq} - \Delta h_m$ depends on both p/q and Δh_M.

For a strongly solvated metal ion (*i.e.*, $(1/p)\Delta H^t_{pq}$ may be largely negative for such a ion), the ion may have a large ordering effect for the solvent molecules even in the secondary solvation shell of the ion, and thus, $(1/p)\Delta S^t_{pq}$ may become less positive. Therefore, the effect due to $(1/p)\Delta H^t_{pq}$ on $(1/p)\Delta G^t_{pq}$ may be compensated by the effect due to $(1/p)\Delta S^t_{pq}$ and thus, the $(1/p)\Delta G^t_{pq}$ value becomes practically independent of metal ions.

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On the Ag(II, I) and Co(III, II) Standard Redox Potentials

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Investigating the solution chemistry of transition metal ions in high oxidation states, at low temperature (–5 °C) and in strongly acidic medium (5 *M* $HClO_4$), our first success was, the evaluation of the standard redox potential of the Ag(II, I) pair. This is the e.m.f. of the hypothetic cell:

$$Au/Ag^{2+}, Ag^+, H^+, ClO_4^- = 5\,M/H_2\ (1\ atm), Pt \qquad (R)$$

at –5 °C, with $[Ag^{2+}] = [Ag^+]$, $C_{HClO_4} \to 5M$, and E = O for the half cell: Pt, H_2 (1 atm)/H^+ (a = 1). Owing to the experimental impossibility of building such a cell, and thanks to the good working of the glass electrode in such conditions [1], we measured the e.m.f.s of the cells without junction:

$$G.E./HClO_4\ 5M/H_2\ (1\ atm), Pt \qquad (H)$$

and

$$Au/Ag^{2+}, Ag^+, H^+, ClO_4^- = 5\,M/G.E. \qquad (G)$$

whose combination and rearrangement leads to:

$$E_R - K\log[Ag^{2+}]/[Ag^+] + K\log[H^+] = \\ = E^\circ_{Ag^{2+}/Ag^+} + K\log F = E^\circ \qquad (1)$$

where F is the activity coefficients ratio and all concentrations are expressed in molality. All the terms on the left side of eqn. (*1*) are directly measurable, while we call standard redox potential of the Ag(II,I) pair, at –5 °C and in 5 *M* $HClO_4$ (6.5 *M*), the sum of the right side terms.