

In a related dinitrogen complex of iron(0), $[\text{Fe}(\text{N}_2)(\text{dmpe})_2]$ ($\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$), formed upon deprotonation of $[\text{FeH}(\text{N}_2)(\text{dmpe})_2]^+$ by KOBut , it was shown [4] that N_2 undergoes protic cleavage (e.g., by HCl) to ammonia. However, in contrast with this entirely chemical reduction of N_2 , the observed methylisocyanide reduction in our study followed an electrochemical route.

Final comments

This work indicates that an alkyl isocyanide ligand at an iron centre can undergo electrochemical activation towards protonation to give a dialkylamine, in a process which possibly involves the formation of a coordination iron(0) centre. Attempts to isolate and characterize intermediates in this process are under way.

The observed reduction of methylisocyanide to dimethylamine involves a 4-electron process which is also known to occur in nitrogenase. However, a 6-electron reductive pathway can also be followed in the enzymatic system, a situation which we have achieved previously [5] in the electrochemical reduction of CNMe at some thiomolybdate-derived centres, with formation of ammonia, methane and ethylene, involving the cathodic CN bond cleavage, a process which has not been detected at our iron system.

References

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IONIC INTERACTIONS IN PHOSPHATE AQUEOUS SOLUTIONS

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Abstract

Mean activity coefficients of NaCl have been calculated, by means of the Pitzer theory, in mixed solutions of NaCl and NaH_2PO_4 and of NaCl and Na_2HPO_4 , with ionic strength lower than 2 mol kg^{-1} , at 25°C . Electromotive force measurements, using a silver, silver chloride and a sodium ion selective electrodes, show nernstian response, in those mixed electrolyte solutions.

Introduction

In the study of mixed electrolyte solutions, the Pitzer approach separates arbitrarily between electrostatic and specific short-range interactions, and enables these, expressed as virial coefficients, to be calculated for single electrolyte solutions and applied to the analysis of mixtures [1]. Aqueous phosphate solutions are of great interest, mainly because phosphates are present in many natural waters, effluents and physiological fluids, being the sodium chloride the predominant electrolyte in some of them. The mean activity coefficient of NaCl has been calculated, by means of the Pitzer theory, in solutions of NaCl and NaH_2PO_4 and of NaCl and Na_2HPO_4 , and electromotive force measurements on the cell



have been used to study the response of the silver, silver chloride and sodium ion selective electrodes in those mixed electrolyte solutions.

Equations

According to the Pitzer treatment, the mean activity coefficient of NaCl, in mixed solutions of NaCl and NaH₂PO₄, is given by

$$\ln \gamma_{\text{NaCl}} = F1 + (m_{\text{Na}} + m_{\text{Cl}}) B_{\text{NaCl}} + m_{\text{H}_2\text{PO}_4} B_{\text{NaH}_2\text{PO}_4} + m_{\text{H}_2\text{PO}_4} \Theta_{\text{Cl}, \text{H}_2\text{PO}_4} + m_{\text{Na}} m_{\text{Cl}} B'_{\text{NaCl}} + m_{\text{Na}} m_{\text{H}_2\text{PO}_4} B'_{\text{NaH}_2\text{PO}_4} \quad (1)$$

where m represents the molality of the species indicated in subscript, B is the second virial coefficient relative to the single electrolyte, B' is its derivative and Θ represents the second virial coefficient relative to the mixture. The quantities B and B' are expressed as $B = \beta^{(0)} + \beta^{(1)} \cdot F2$ and $B' = \beta^{(1)} \cdot F3$ and $F1$, $F2$ and $F3$ are functions of the ionic strength:

$$F1 = -0.392 \left[\sqrt{I}/(1 + 1.2\sqrt{I}) + (2/1.2) \ln(1 + 1.2\sqrt{I}) \right] \quad (2)$$

$$F2 = [1/(2I)] [1 - (1 + 2\sqrt{I}) \exp(-2\sqrt{I})] \quad (3)$$

$$F3 = [1/(2I^2)] [-1 + (1 + 2\sqrt{I} + 2I) \exp(-2\sqrt{I})] \quad (4)$$

In a mixed solution of NaCl and Na₂HPO₄, γ_{NaCl} is also given by equation (1) with H₂PO₄ replaced by HPO₄. The β values for NaCl and Na₂HPO₄ and $\Theta_{\text{Cl}, \text{H}_2\text{PO}_4}$ are known from isopiestic data and from a recalculation of pK₁ of H₃PO₄ [1] and $\beta^{(0)}_{\text{NaH}_2\text{PO}_4}$, $\beta^{(1)}_{\text{NaH}_2\text{PO}_4}$, and $\Theta_{\text{Cl}, \text{HPO}_4}$ were obtained from studies on the second dissociation of H₃PO₄ [2]. In these equations the third virial coefficients have been omitted, since they are not relevant for moderately concentrated solutions.

Experimental

Aqueous solutions were prepared by weight, using NaCl from Merck p.a., NaH₂PO₄ from Fluka Puriss. and Na₂HPO₄ from BDH AnalaR, dried in an oven, at 110 °C, and kept in a dessiccator. The silver, silver chloride electrodes were of the thermal-electrolytic type and the sodium ion selective electrode was a commercial one, Metrohm AG, model 6.0501.100. The measurements were done on a digital potentiometer, Metrohm 654, with the solutions immersed

in a thermostated bath (Selecta, Digiterm, model 3000613), at 25 °C. The temperature was kept constant within ± 0.01 °C. Four sets of measurements were performed, the NaCl molality being 0.05, 0.15, 0.5 and 1.0 mol kg⁻¹ and the ionic strength was increased by adding Na₂HPO₄ to the first two sets of solutions and NaH₂PO₄ to the last two, respectively.

Results and Discussion

The mean NaCl activity coefficient, calculated by means of equation (1), is represented in figures 1 and 2, as a function of the ionic strength, I . The three curves correspond to NaCl mole fractions of 1, 0.5 and 0. Using the same equation, the NaCl activity in the solutions prepared for cell (I) was calculated and a linear variation of the e.m.f.(E) with $\log a_{\text{NaCl}}$ was observed, as shown in figures 3 and 4.

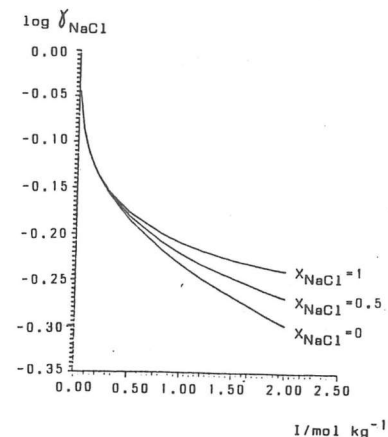


Figure 1: The activity coefficient of NaCl in NaCl + NaH₂PO₄ solutions

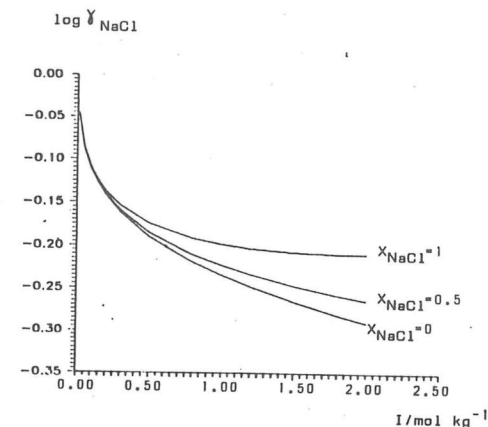


Figure 2: The activity coefficient of NaCl in NaCl + Na₂HPO₄ solutions

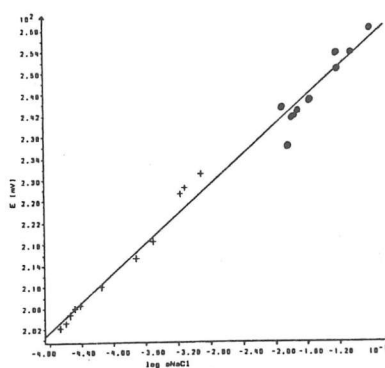


Figure 3- Variation of e.m.f. of
cell (1) with NaCl + NaH₂PO₄:
+ NaCl 0.5m; ● NaCl 1.0m

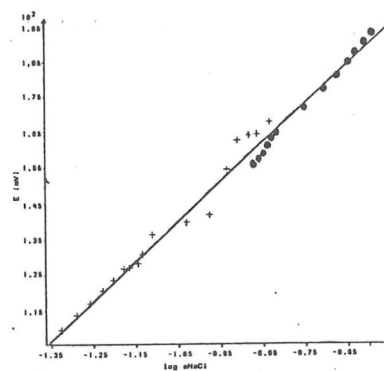


Figure 4- Variation of e.m.f. of
cell (1) with NaCl + Na₂HPO₄:
+ NaCl 0.05m; ● NaCl 0.15m

There are still problems in the application of Pitzer equations, specially at higher concentrations, since some of the coefficients are not known. This method does not seem very appropriate in determining all Pitzer coefficients, as the potential differences, caused by the exchange of some Cl⁻ ions by H₂PO₄⁻ or HPO₄²⁻ are quite small and need to be evaluated very accurately.

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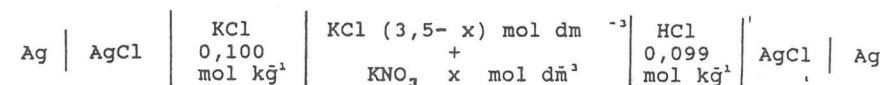
STUDY OF LIQUID JUNCTION POTENTIALS WITH MIXED BRIDGE SOLUTIONS

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Summary: Liquid junction potentials between 0,099 mol kg⁻¹ HCl and 0,100 mol kg⁻¹ KCl were measured without and with bridge solutions. Ag, AgCl electrodes of the thermal electrolytic type and a novel cell design with liquid junction formed in a capillary tube with cylindrical geometry were used. The results were compared with calculated and experimental values obtained with a similar system but more complicated than the present one.

Fizeram-se determinações experimentais de potenciais de junção líquida em sistemas com ponte salina mista, com o intuito de se implementarem as condições para o estabelecimento de junções deste tipo que pudessem contribuir de forma bem definida para determinações potenciométricas em sistemas que as envolvam.

O sistema estudado foi o seguinte:



e os resultados obtidos foram comparados quer com os já publicados por Finkelstein utilizando um sistema semelhante [1], quer com os calculados pelas equações de Henderson [2] e de Harper [3].

COMPARAÇÃO COM OS RESULTADOS DE FINKELSTEIN

O nosso estudo baseou-se no de Finkelstein [1] embora tenham sido introduzidas algumas modificações, com o objectivo de melhorar o sistema, nomeadamente, no que diz respeito ao vaso da célula e aos eléctrodos.

No vaso da célula utilizado neste trabalho (que corresponde ao obtido por Rebelo [4]), a junção também é de simetria cilíndrica mas tornava-se mais funcional devido ao seu design mais simples.

Quanto aos eléctrodos, optou-se pelos de prata-cloreto de prata em vez dos de calomelanos, e consequentemente os sistemas atingiam o equilíbrio muito mais rapidamente (4 h em vez de 8,5 h, referidas em [1]).