Equations of State for Electrolytes

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1. Introduction

- Activity Coefficient Model
  - An inconsistency when electrostatic terms are improperly superimposed on convential Gibbs model.

    Cardoso and O'Connell(1987)
  - The systems containing supercritical components at high pressures
    - Not possible to select a truly useful standard state for the supercritical components(Pausnitz et al., 1986)

- Equation of State(Helmholtz energy framework)
  - To calculate the fugacity(of chemical potential) of each species in each phase
  - To be successful for nonelectrolyte systems
  - The problem is to superimpose properly the electro-static effects in an EOS for nonelectrolyte systems.

2. Review on Electrolyte Equation of States

- Raatschen’s model(1987)
  - Debye-Huckel, Born and Pitzer term for ionic contributions
  - Not to be in a form suitable for extension to systems containing supercritical gases
- Copeman and Stein(1987)
  - To use MSA model to describe ion-ion interactions
  - To be limited to pressures near atmospheric
  - To need second parameter for highly concentrated systems

- Jin and Donohue(1988, 1991)
  - PACT model for short-range molecule-molecule interactions
  - The perturbation expansion for long-range Coulombic interactions
  - Adjustable parameter
    - One parameter for each electrolyte(1988)
    - The ionic radii for each ion(1991)
  - To apply the supercritical gases and the salt systems

- Harvey and Prausnitz(1989)
  - $A = A^{I} + \Delta A^{II} + \Delta A^{III}$
    - A^{I} is the "nonelectrolyte" contribution from Barker-Henderson perturbation theroy.
    - ΔA^{II} is the ion-charging contribution.
      - $\Delta A^{II} = \dfrac{N_A e^2}{RT} \sum_i x_i z_i^2 \left(\dfrac{1}{D\sigma_{c,i}} + \dfrac{1}{\sigma_{ii}} - \dfrac{1}{\sigma_{c,i}} \right)$
      - To produce the effect on the fugacities of the uncharged species through the composition dependence of the dielectric constant
      - To account for long-range portions of the ion-solvent interacions

Harvey and Prausnitz(1989) (II)

- ΔA^{III} accounts for charge-charge interactions

$$\Delta A^{III} = -\frac{(2\Gamma)^3(1+1.5\sigma_{mix}\Gamma)}{12\pi N_A \rho}$$

  - To approximate the Blum's MSA model for iterative equation of state calculations

◆ Binary parameter(k_{ij})

- To consider the solvent/ion interactions
- To correct the salting-out effect
  - Utilization of Setchenow-constant data

Harvey and Prausnitz(1989) (Result)

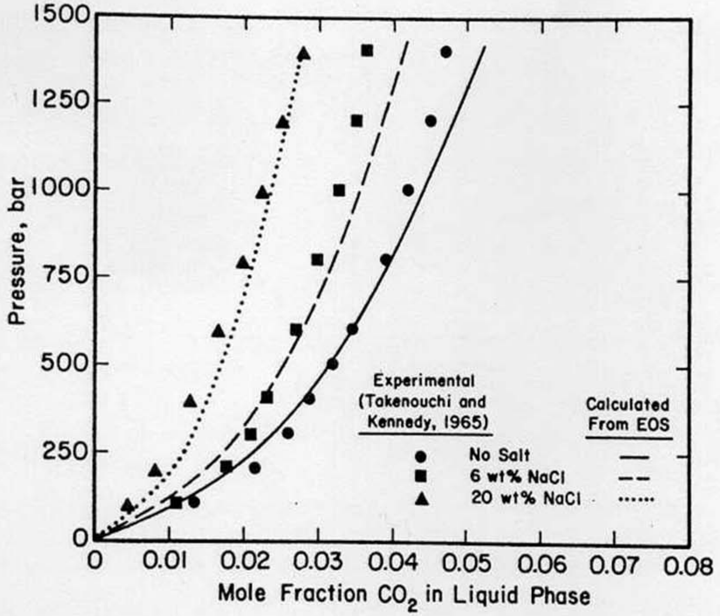

Figure 2. Salting-out of carbon dioxide by sodium chloride at 150°C.

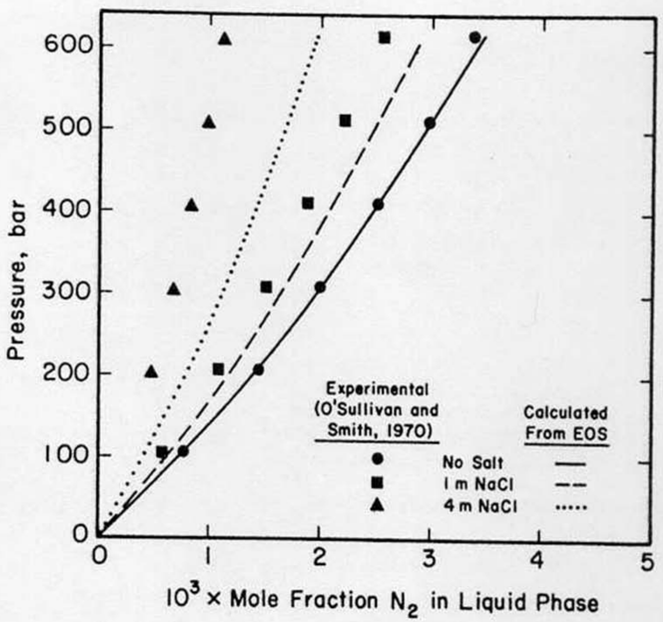

Figure 4. Salting-out of nitrogen by sodium chloride at 102.5°C.

- Harvey and Prausnitz(1989) (Discussion)
  - The MSA is the lowest-order term in series
  - The ion/water interaction is not described correctly at high salt concentrations
  - The salt/water and salt/gas binary parameters may be dependent on temperature
  - The nonelectrolyte portion of the EOS would improve the salt-free systems.(hydrogen-bonding and structural effects in water)

- Aasberg-Petersen et al(1991)
  - $\ln \phi_i = \ln \phi_i^{EOS} + \ln \gamma_i^{EL}$
  - The EOS part (Cubic EOS) is evaluated by using the salt-free mole fractions.
  - Activity coefficients are calculated by Debye-Huckel model.(Macedo et al., 1990)
    - $\ln \gamma_i^{EL} = \dfrac{2Ah_{is}M_m}{B^3} f(BI^{1/2})$
    - binary parameter, h_{is} (water/salt, salt/gas)

- Aasberg-Petersen et al(1991)(Result)

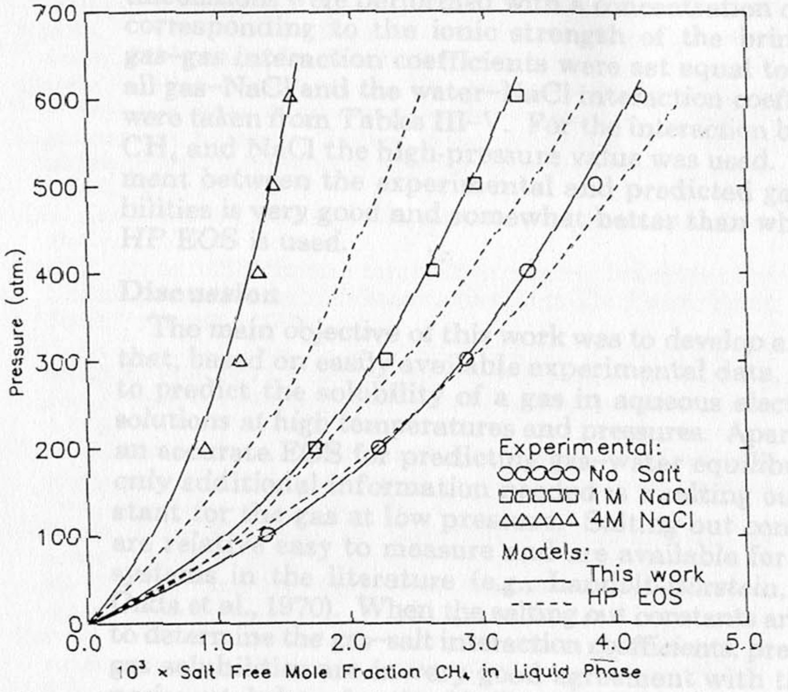

Figure 3. Experimental and calculated pressures *versus salt free* mole fractions of CH_4 in water and aqueous mixtures of NaCl using the HP EOS and the model presented in this work; T = 375 K.

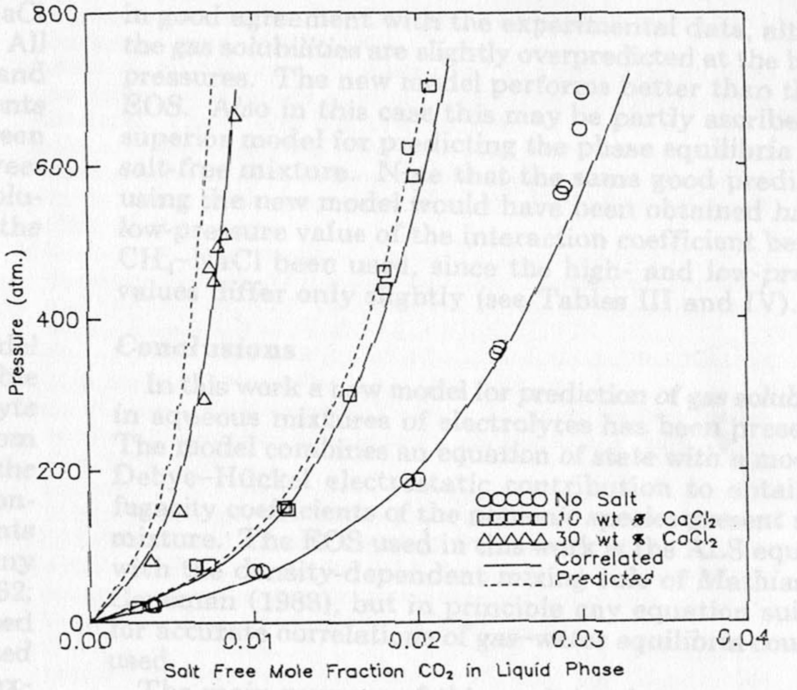

Figure 5. Experimental and calculated pressures versus salt free mole fractions of CO_2 in water and aqueous mixtures of $CaCl_2$; T = 394 K.

- Furst and Renon(1993)(Theory)

$$\left(\frac{a-a^0}{RT}\right)=\left(\frac{a-a^0}{RT}\right)_{RF}+\left(\frac{a-a^0}{RT}\right)_{SR1}+\left(\frac{a-a^0}{RT}\right)_{SR2}+\left(\frac{a-a^0}{RT}\right)_{LR}$$

◆ $$\left(\frac{a-a^0}{RT}\right)_{RF}+\left(\frac{a-a^0}{RT}\right)_{SR1}=\sum_k x_k \ln\frac{x_k RT}{P_0(v-b)}+\frac{a^{SR}}{RT(b+c)}\ln\frac{v+c}{v+b+2c}$$

  - Schwartzentruber et al.(1989)
  - Repulsive forces(RF) and the first attractive short-range forces term(SR1)
  - Wong-Sandler mixing rule using UNIQUAC or NRTL

Furst and Renon(Theory)

- $$\left(\frac{a-a^0}{RT}\right)_{SR2} = -\sum_k \sum_l \frac{x_k x_l W_{kl}}{v(1-\xi_3)} \qquad \xi_3 = \frac{N\pi}{6}\sum_k \frac{x_k \sigma_k^3}{v}$$
  - A short-range term specific to interactions involving ionic species
- $$\left(\frac{a-a^0}{RT}\right)_{RF} = -\frac{\alpha_{LR}^2}{4\pi}\sum_k \frac{x_i Z_i^2 \Gamma}{1+\Gamma\sigma_i} + \frac{\Gamma^3 v}{3\pi N}$$
  - where the shielding parameter Γ is obtained from

$$4\Gamma^2 = \alpha_{LR}^2 N \sum_i \frac{x_i}{v}\left(\frac{Z_i}{1+\Gamma\sigma_i}\right)^2$$

  - The long-range interaction term in the form used by Ball

Furst and Renon(Theory)

- Ionic parameters(b_i, σ_i, W_{kl})
  - $\sigma_i = \sqrt[3]{\dfrac{6b_i}{N\pi}}$
  - $b_c = \lambda_1\left(\sigma_c^S\right)^3 + \lambda_2, \quad b_a = \lambda_1\left(\sigma_a^P\right)^3 + \lambda_2$
  - $W_{cw} = \lambda_3\sigma_c^S + \lambda_4$
  - $W_{ca} = \lambda_5\left(\sigma_c^S + \sigma_a^P\right)^4 + \lambda_6$
    - Adjustable parameter : λ_5, λ_6

- Furst and Renon(1997)
  - Apply to the nonaqueous solvent-salt systems
  - Predict the vapor pressures and the mean ionic activity coefficients
- Zuo and Renon(1998)
  - Apply to the calculation of VLE and mean ionic activity coefficients for mixed solvent electrolyte system

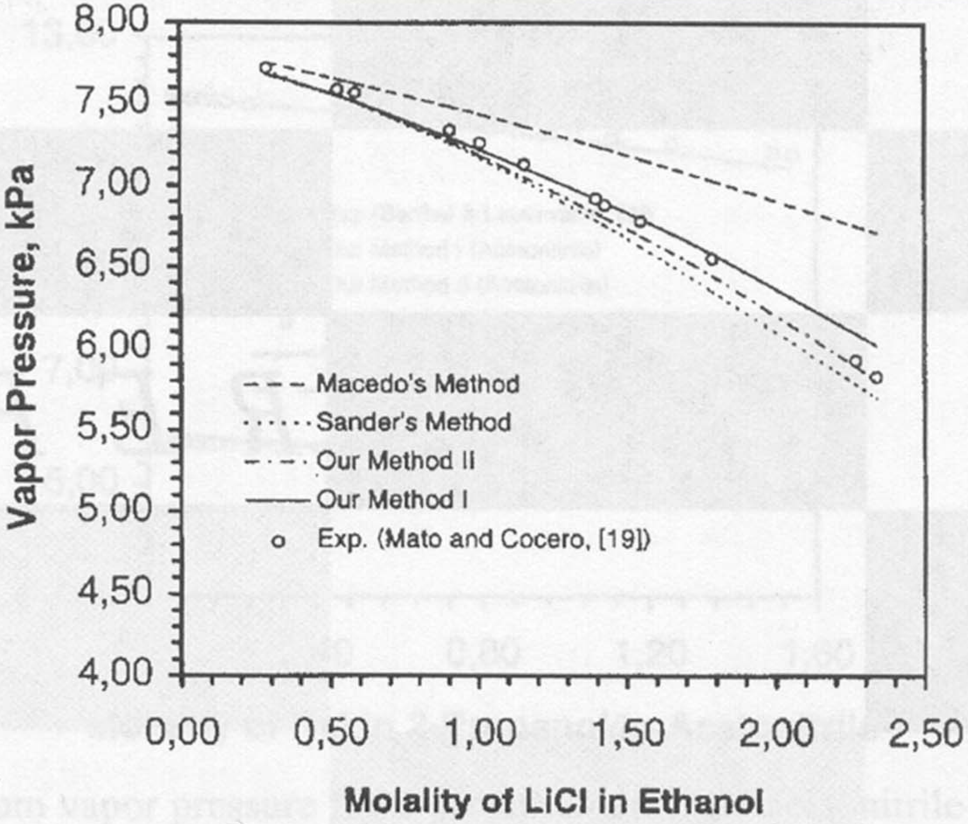

Fig. 3. Representation of equilibrium vapor pressure for ethanol–LiCl system at 298.15 K.

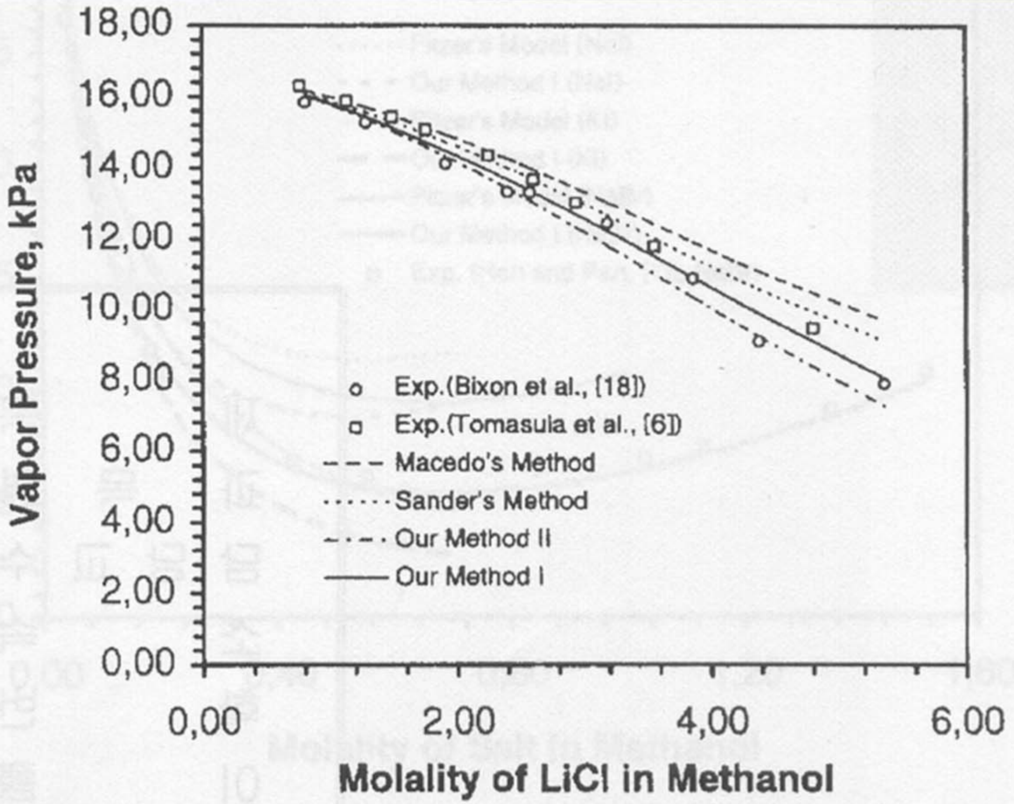

Fig. 4. Representation of equilibrium vapor pressure for methanol–LiCl system at 298.15 K.

- Zuo et al(FPE, 2000)
  - Extension to mixed solvent halide electrolyte systems
- Zuo et al(Energy and Fuels, 2000)
  - Represent hydrate phase equilibria in aqueous solutions of methanol and electrolytes using the Furst and Renon model

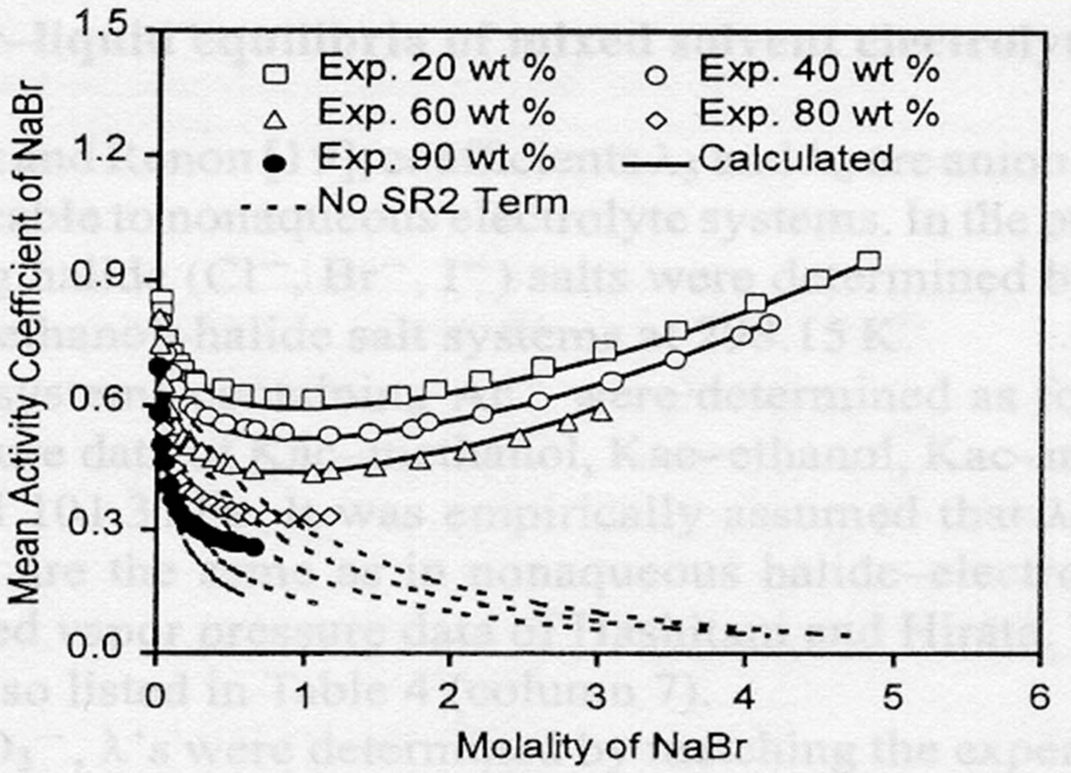

Fig. 5. Mean activity coefficients of NaBr in water–ethanol mixtures at 298.15 K.

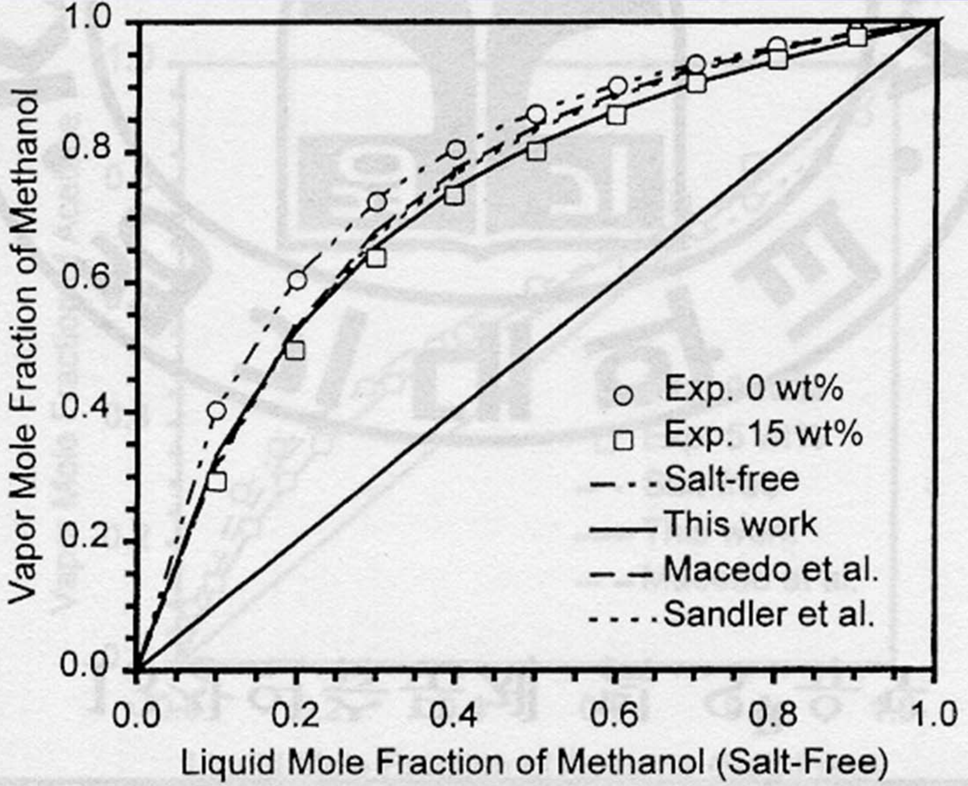

Fig. 8. Vapor–liquid composition diagram for the methanol–1-propanol–$CaCl_2$ system at 298.15 K.

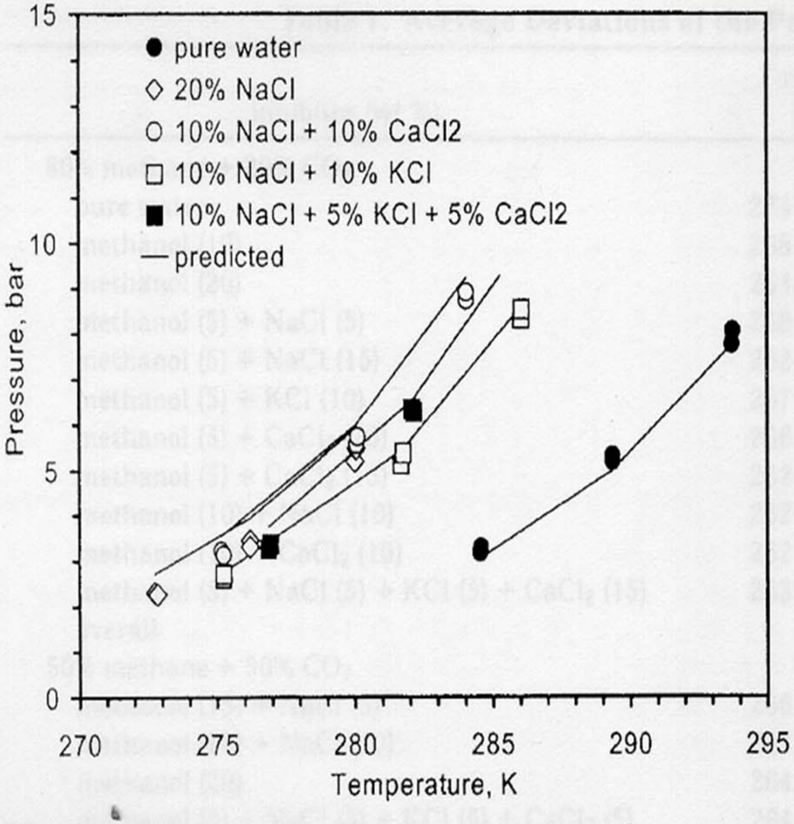

Figure 1. Hydrate formation conditions of H_2S in aqueous electrolyte solutions (experimental data: Bishnoi et al.[3]).

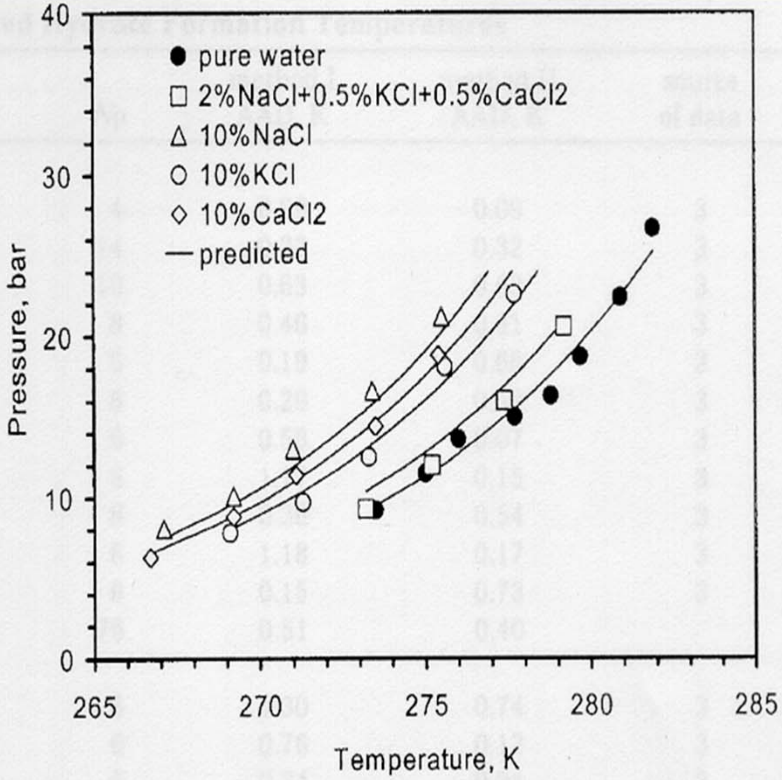

Figure 2. Hydrate formation conditions of synthetic natural gas in aqueous electrolyte solutions (experimental data: Mei et al.[4]).