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Purification of Natural gas: Thermodynamics of Alkanolamine - Water System

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ABSTRACT

Present study is focused on thermodynamics of binary MEA- H₂O, DEA- H₂O, and MDEA- H₂O systems, which is required to predict the vapour-liquid equilibrium of acid gas – aqueous alkanolamine systems. Determination of binary interaction parameters, prediction of infinite dilution activity coefficient, heats of solution at infinite dilution and the excess Gibbs free energy and excess enthalpy for binary alkanolamine-water systems are the objectives of this study.

INTRODUCTION

The removal of acid gas impurities such as CO₂ and H₂S, using alkanolamines requires the knowledge of vapour-liquid equilibrium of acid gas – aqueous alkanolamine systems. To model the thermodynamics of acid gas-alkanolamine-water systems, we must understand the constituent binary systems such as (Alkanolamine - water) system, which is a single weak electrolyte system.

In this work, the Margules expression, a semi empirical excess Gibbs energy model has been used to model the physical equilibrium of MEA- H₂O, DEA- H₂O, and MDEA- H₂O systems. The binary interaction parameters along with their temperature dependence obtained from the regression analysis using freezing point depression, heat of mixing, and the total pressure data available in the literature for alkanolamine-water systems, are then included to model the ternary (acid gas – alkanolamine – water) systems without further regression. The relationship between each data type and the model parameters is different. The analytical and thermodynamically exact form of the infinite dilution activity coefficient of alkanolamines obtained using the Margules parameters, have been used to predict the infinite dilution activity coefficients for the alkanolamines considered, which finds application in

normalization of activity coefficients. The prediction of heats of solution at infinite dilution for MDEA, DEA and MEA have been done with the margules parameters. Present work is also focused on the prediction of non-ideality of alkanolamine-water systems in relation to the excess Gibbs free energy and excess enthalpy and the temperature effect on them.

MODEL STRUCTURE

As the concentration of the ions approaches zero, in the modified Clegg-Pitzer equations, used elsewhere by the present authors to represent the VLE of the ternary (acid gas-alkanolamine-water) system, this model reduces to Margules expression. With linear format and the flexibility in the number of terms included, Margules model is able to represent available data within experimental uncertainty and without serious computational burden. It was therefore logical to model the binary alkanolamine systems using Margules model. The Margules expression, a semi empirical excess Gibbs energy model, has the following form for the binary system:

$$\frac{G^{ex}}{RT} = x_1 x_2 (A_{21} x_1 + A_{12} x_2) \quad (1)$$

where $A_{12}=a_{12}+\frac{b_{12}}{T}$, $A_{21}=a_{21}+\frac{b_{21}}{T}$

x_1 and x_2 are the liquid phase mol fractions of component 1 and 2 respectively. The expression for the activity coefficient for component 1 in the binary mixture is,

$$\ln \gamma_1 = x_2^2 \left(A_{12} + 2(A_{21} - A_{12}) x_1 \right) \quad (2)$$

By taking the limit as the mol fraction of amine approaches zero, the infinitely dilute amine activity coefficient becomes

$$\ln \gamma_{\text{amine}}^\infty = a_{12} + \frac{b_{12}}{T} \quad (3)$$

It is evident from eqs (1) and (2) that the excess Gibbs energy and the activity coefficients are related to the model parameters. The relationship between each data type and the model parameters is different and they are described separately.

Total pressure data

For alkanolamine-water binary system the following equation can be used to represent equilibrium for total pressure data. Pressures of amine water data are usually low enough to neglect gas phase non-idealities.

$$P = \gamma_i p_i^0 x_i + \gamma_j p_j^0 x_j \quad (4)$$

Where, P is the total solution vapour pressure, p_i^0 is the Antoine pure vapour pressure of component i , x_i is the mol fraction of component i , and γ_i is the symmetric activity coefficient of component i . The model parameters are varied to change the calculated activity coefficients in order to fit the total pressure data.

Freezing point depression data

The activity of water is related to the freezing point depression of water.

$$-\ln(a_w) = \left(\Delta H_f / RT_0^2 \right) \Delta T_f + \left(\Delta H_f / RT_0 - \Delta C_p / 2R \right) \Delta T_f^2 / T_0^2 \quad (5)$$

Where T_0 is the normal freezing point of water ΔT_f is the change in freezing of water, ΔH_f is the heat of fusion of water,

and ΔC_p is the difference in heat capacity between water and ice.

$$\gamma_w = \exp(-0.018 \Delta T_f / 1.858) / x_w \quad (6)$$

Freezing point depression data quantifies the activity coefficients of amine water system, which are required to predict acid gas solubility accurately at low loading. Its combination with total pressure data, which covers a wide range of temperature and concentration, should develop reliable amine - water parameter to predict acid gas solubility at industrially important conditions.

Excess enthalpy data

Excess enthalpy is defined here as the isothermal enthalpy change per mol of solution when two pure liquids mix without a chemical reaction. Excess enthalpy data is useful for modeling because it is directly related to the temperature dependence of excess Gibbs energy as follows.

$$d(G^{\text{ex}}/RT)/d(1/T) = -h_{\text{ex}}/R \quad (7)$$

Therefore, in Gibbs energy model for activity coefficients excess enthalpy measurements will provide more accurate temperature dependence for the model. Eq (8) illustrates the relationship of excess enthalpy to the parameters of the model.

$$h_{\text{ex}}/R = x_1^2 x_2 b_{21} + x_1 x_2^2 b_{12} \quad (8)$$

Data regression and determination of interaction parameters

The binary interaction parameters for (alkanolamine + H₂O) system are determined by the regression analysis of the combined set of freezing point depression (Chang *et al.*, 1993) and total pressure data (Nath and Bender, 1983) of aqueous solutions of alkanolamines. The average correlation deviations for aqueous MEA, DEA, and MDEA systems were 2.942 %, 2.995%, and 3%, respectively. Best estimates of the parameters are reported in Table 1.

RESULTS AND DISCUSSION

The symmetrically normalized water and amine activity coefficient in aqueous MEA, DEA and MDEA solutions have been calculated and is presented in Figures 1 and 3 along with the NRTL prediction for MDEA-H₂O and DEA-H₂O system respectively. In the dilute solution range, which is industrially important, the

water activity coefficient is close to unity and the amine activity coefficients deviate significantly from unity for all the alkanolamines. An infinite dilution, the activity coefficient value for MDEA is greater than 1.0, which is unique among all the alkanolamines studied. Chang *et al.* (1993) reported the same trend at 393 K by using UNIFAC group contribution method.

Infinite dilution amine activity coefficient

Using the Margules parameters, the infinite dilution amine activity coefficients have been calculated (using eq (3)) for MEA, DEA and MDEA and converted into the common temperature dependent form as shown in Table 2.

Heat of mixing

The temperature effect on the infinite dilution amine activity coefficient is directly related to the heat of mixing of pure amine solution based on the infinite dilution reference state.

$$\frac{d(\ln \gamma_{\text{amine}}^{\infty})}{d(1/T)} = b_{12} = \frac{\Delta h_{m,\text{pure}}^{\infty}}{R} \quad (9)$$

Eq (9) has been used to calculate the heats of solution at infinite dilution for MEA, DEA, and MDEA using the Margules parameters and are presented in Table 3.

Non-ideality of alkanolamine - water system

Excess Gibbs free energy

The excess Gibbs free energy has been calculated using the binary interaction parameters. The relative solution non-ideality of various aqueous alkanolamines (Figure 4) at 273, 313 and 393 K are as follows,

(MEA-H₂O) < (MDEA-H₂O) < (DEA-H₂O)

(MEA-H₂O) < (MDEA-H₂O) < (DEA-H₂O)

(MEA-H₂O) ≈ (MDEA-H₂O) < (DEA-H₂O)

Excess enthalpy

Figure 2 shows the predicted excess enthalpies of aqueous MEA DEA and MDEA solutions along with the experimental measurements of Posey (1996) at 298 K. Temperature extrapolations of the (amine-water) behaviour without the use of heat of mixing data can lead to serious errors.

CONCLUSION

Thermodynamics of alkanolamine-water system have been predicted here keeping in view of its immense significance in rigorous thermodynamic modeling of VLE of acid gas- alkanolamine-water systems. Binary alkanolamine-water interaction parameters have been determined using thermodynamic data such as freezing point depression, heat of mixing apart from total pressure data. Infinite dilution activity coefficients of MEA, DEA, and MDEA in water and their temperature dependence have found out. The agreement between the predicted and experimental values of heats of solution at infinite dilution, available in the literature further establishes the appropriate determination of the binary alkanolamine-water interaction parameters in the present work. The analytically derived values of excess Gibbs energy and excess enthalpy at different temperatures have been able to describe the solution non-ideality for the aqueous alkanolamines considered in this work.

ACKNOWLEDGEMENT

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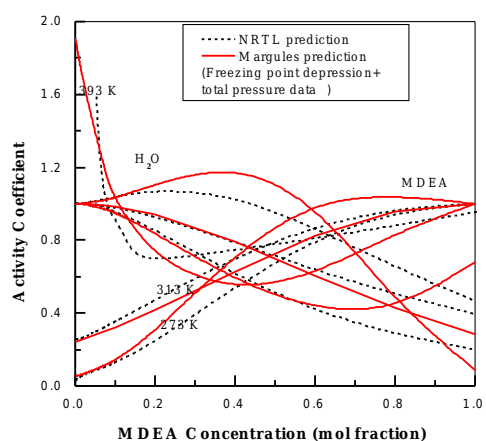


Figure 1. Representation of MDEA and water activity coefficient in aqueous MDEA

solution in the temperature range 273-393 K.

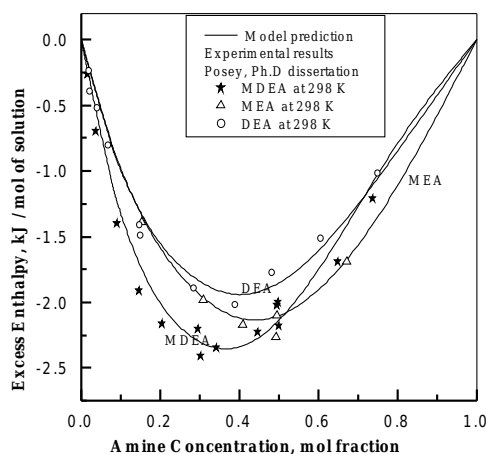


Figure 2. Representation of excess enthalpy at 298 K

Table 1. Fitted values of the Margules interaction parameters for alkanolamine-

Alkanolamine	c_{12}	d_{12}	c_{21}	d_{21}	AAD % Error
MEA	1.2780	-814.5323	1.7837	-842.2123	2.94
DEA	-0.7890	-217.6363	-0.7225	-59.7158	2.995
MDEA	8.780443	-3196.153	-7.19149	1857.67	3.0

Table 2. Temperature dependence of the amine activity coefficient at infinite dilution in water

Alkanol-amine	A	D	C	D
MEA	-12.615772893	-172.6622214	2.094818654136	-0.00062239449
DEA	-0.37843412883	-0.633489227	-0.34936948753	0.002884699584
MDEA	-0.56004606453	-7.815696823	0.104665882509	-0.00009831352
		73	58	22
		57	4	35
		24	76	

Table 3. Infinitely dilute heats of solution of MEA, DEA, and MDEA at

Alkanolamine	$\Delta H_{\text{soln}}^{\infty}$ (kJ / mol solution)		
	Present work	Kim et al.	Chang et al.
MEA	-6.76 ^a (-11.55 ^b)	-11.43	-10.1
DEA	-1.81 ^a (-11.98 ^b)	-14.50	-3.3
MDEA	-26.55 ^a (16.4 ^b)	-20.5	-27.3

^aBased on Megules parameter derived by regression analysis of freezing point depression and total pressure data

^bBased on Margules parameter derived by regression analysis on the combined set of freezing point depression, total pressure, heat of mixing and VLE data for MEA and freezing point depression, total pressure, and heat of mixing data for DEA and MDEA respectively, at 298 K.

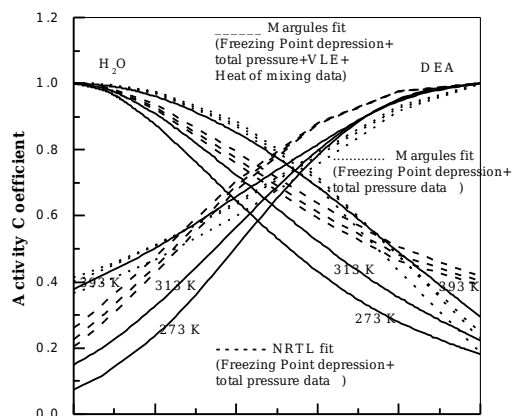


Figure 3. Representation of DEA and water activity coefficient in aqueous DEA solution

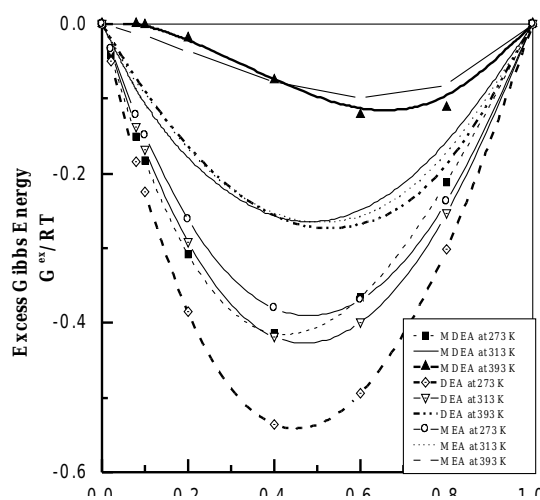


Figure 4. Representation of excess at 273 and 313 K