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A STUDY OF PHASE EQUILIBRIUM OF H_2S IN SEVERAL PHYSICAL SOLVENTS USING CHEMCAD SIMULATOR

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ABSTRACT

CHEMCAD process simulator was used for the analysis of the literature experimental phase equilibrium data of H_2S with three physical solvents (Sulfolane, Propylene Carbonate (PC), and N-Methyl-2-Pyrrolidone (NMP)) at different temperatures (298.15 ^oK , 323.15 ^oK, and 373.15 ^oK). Two thermodynamic models, Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK), were used.

The equilibrium data of H_2S- Sulfolane and H_2S- Propylene Carbonate (PC) systems were successfully correlated using SRK thermodynamic model. The deviation was noticed only for H_2S-Sulfolane system as the temperature increases to 373 ^oK, to give a deviation of less than 5% .

The thermodynamic models used in present study, PR, and SRK , built in CHEMCAD simulator and used as such without modification, fail to correlate the equilibrium data of H_2S- NMP (N-Methyl-2-Pyrrolidone) system for all temperature range used.

Modifications of the thermodynamic models were performed by editing user defined binary interaction parameters (BIP) of the systems used, gives good results.

KEYWORDS

Vapor–Liquid Equilibria, H_2S, Physical Solvents, CHEMCAD Simulator, Thermodynamic Models, Equation of state and correlation

NOMENCLATURE

$\mathbf{A_{ij}}$	Constant of the binary interaction parameter correlation	-
$\mathbf{B_{ij}}$	Constant of the binary interaction parameter correlation	-
$\mathbf{C_{ij}}$	Constant of the binary interaction parameter correlation	-
$\mathbf{K_{ij}}$	the binary interaction parameter between component i & j	-
K	Equilibrium constant	Bar
P	Pressure	Bar
T	Temperature	^oK
X	H_2S mole fraction in liquid phase	-
γ_i	the activity coefficient	

ABBREVIATIONS

NRTL	Non-Random Two-Liquid Equation based on activity coefficient Equilibrium thermodynamic model recommended for Polar (Highly Non-Ideal Solutions)
PR	Peng-Robinson thermodynamic model to calculate K-values, based on equation of state recommended for most hydrocarbon systems
SRK	Soave-Redlich-Kwong thermodynamic model to calculate K-values , based on equation of state recommended for most hydrocarbon systems
UNIFAC	UNIQUAC Functional-Group Activity Coefficient Equilibrium thermodynamic model recommended for Polar (Highly Non-Ideal Solutions) , used where data is absent.
UNIQUAC	Activity Coefficient Equilibrium thermodynamic model recommended for Polar (Highly Non-Ideal Solutions)

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INTRODUCTION

One of the major sections of any process simulation software is the physical properties & thermodynamic model selection. CHEMCAD simulator data base included more than 1800 components, with more than 6000 binary data from the DECHEMA data bank. Other sources for vapor-liquid equilibrium, in combination with mixing rules and more than twenty thermodynamic models like Peng-Robinson (PR) , Soave-Redlich-Kwong (SRK), NRTL, UNIQUAC, UNIFAC, Henry, etc., provide the ideal means to easily model processes.[1]

The design of separation processes strongly depend on accurate vapor–liquid equilibrium data. Extreme care must be exercised in choosing a model for phase equilibria (some times called the fugacity coefficient, K-factor, or fluid model). Whenever possible, phase equilibrium data for the system should be used to regress the parameters in the model, and the deviation between the model predictions and the experimental data should be studied. [2]

There are two general types of fugacity models;

1. Equation Of State (EOS) Models

An equation of state is an algebraic equation for the pressure of a mixture as a function of the composition, volume, and temperature. Through standard thermodynamic relationships, the fugacity, enthalpy, and so on, for the mixture can be determined. These properties can be calculated for any density; therefore, both liquid and vapor properties can be calculated. The most popular equations of state are PR (Peng-Robinson) and SRK (Soave-Redlich-Kwong). They normally use three pure-component parameters per substance and one binary-interaction parameter per binary pair. The predicted phase equilibrium is a strong function of the binary-interaction parameters (BIPs).[2]

2. Liquid-State Activity-Coefficient Models

Activity-Coefficient Models, however, can only be used to calculate liquid state fugacities and enthalpies of mixing. These models provide algebraic equations of the activity coefficient (γ_i) as a function of composition and temperature. The activity coefficient is merely a correction factor for the ideal-solution model (essentially Raoult's Law).[2]

The investigation of solublities of gaseous solutes in liquids is of fundamental importance for design of gas absorption processes to purify industrial and natural gases, in petroleum industry, which frequently contain large quantities of carbon dioxide and hydrogen sulfide. The present trend to reduce energy consumption and associated operating expenses together with fulfillment of pollution controls has led to the search for more efficient and economical methods for removing acidic components. Absorption with physical solvents present the advantage of low energy requirements in the regeneration step. Furthermore, they are often preferred for treating gas streams at high pressure with high concentrations of the acid gases (H_2S and CO_2).[3]

Many authors[3-5]reported experimental phase equilibrium data of H_2S with several physical solvents. The present work was undertaken to verify the suitability of the application of CHEMCAD simulator thermodynamic models, in the prediction and correlation of the phase equilibrium of H_2S with a number of physical solvents (Sulfolane, N-Methyl-2-Pyrrolidone (NMP), and Propylene Carbonate (PC)), at different temperatures.

CHEMCAD FOR PHYSICAL PROPERTY CALCULATIONS

To use CHEMCAD Simulator as a physical property calculator, the following steps and procedure can be used:

1. Creation of a New Job

From Tools Bar ; choose the New Job option, Name: PhysProperty , OK

2. Simple Flowsheet Creation

From Edit flowsheet Menu, Construct a small flowsheet with a feed, a flash separator, and two products. Using the Main Palette provides access to the graphics functions and symbols which are necessary for the creation of the flowsheet, as shown in Figure (1).

3. Selection of Engineering Units

From Formate Menu , Eng Units, Alt SI, Save Default, Save Profile, OK.

4. Components Specification

From ThermoPhysical Menu , Component List , [Sulfolane] (449) (Double Click) , [N-Methyl-2-Pyrrolidone] (NMP) (497) (Double Click) , and Propylene Carbonate (PC) (1799) (Double Click) , H_2S (50) (Double Click) , OK .

5. Selection of Thermodynamic Model

From ThermoPhysical Menu , K-Values , Pull down arrow , select PR, or SRK.

6. Editing user defined binary interaction parameters (BIP)

From ThermoPhysical Menu , Databank , BIPS , enter constants A,B, & C.

The binary interaction parameters (BIP) of the PR or SRK thermodynamic model may be correlated as a function of temperature with the following form:

$$K_{ij} = A_{ij} + B_{ij}\,T + C_{ij}\,T^2$$

Where

K_{ij} : is the binary interaction parameter between component i & j .

T : is the temperature , ^oK .

A,B, & C : constants, not all constants are required, if K_{ij} is constant (independent of temperature),only A is existed.

7. Plotting Equilibrium Data

From Menu Bar; Plot , TPXY options , select temperature and the two components required and range of plot.

RESULTS AND DISCUSSIONS

CHEMCAD simulator has been used to correlate the experimental phase equilibrium data of H_2S with three physical solvents (Sulfolane, Propylene Carbonate (PC), and N-Methyl-2-Pyrrolidone (NMP)) at different temperatures (298.15 ^oK , 323.15 ^oK, and 373.15 ^oK), given by the literature, as shown in Tables (1) to (3). Two thermodynamic models (PR, and SRK) were used.

Figures (2) to (4) illustrate the results of H_2S- Sulfolane system. SRK thermodynamic model, built in CHEMCAD simulator and used as such without modification, gives results agree well to the experimental data. Small deviation was noticed (less than 5 %), as the temperature increases and especially at 373.15 ^oK, as shown in figure (4). Whereas Peng-Robinson (PR) thermodynamic model gaves high deviation (higher than 10%).

Figures (5) to (7) show the results of H_2S- Propylene Carbonate (PC) system. SRK thermodynamic model, used as such without modification, gives results agree well to the experimental data for all temperature range used. Whereas Peng-Robinson (PR) thermodynamic model also gave high deviation (higher than 10%).

Figures (8) to (10) show the results of H_2S- NMP (N-Methyl-2-Pyrrolidone) system. The thermodynamic models used in this study (PR, and SRK), used as such without modification, fail to correlate the equilibrium experimental data for all temperature range used. The deviations are higher than 20%.

Modifications of the thermodynamic models were performed on CHEMCAD simulator by editing user defined binary interaction parameters (BIP) of the systems used, especially which gives bad results.

Modified thermodynamic models for H_2S- Sulfolane system are shown in Figures (3) to (4), SRK(0) to SRK(-0.1) and PR(0) to PR(-0.1) give results agree well to the experimental data. The values between brackets are the values of the binary interaction parameters (BIP) K_{ij} .

For H_2S- Propylene Carbonate (PC) system, modified thermodynamic model used is PR(-0.05), gives results agree well to the experimental data, as shown in figures (5) to (7).

For H_2S- NMP (N-Methyl-2-Pyrrolidone) system, modified thermodynamic models used are PR(-0.1), and SRK(-0.1), give results agree well to the experimental data, as shown in figures (8) to (10).

CONCLUSIONS

The following conclusions can be drawn from the present work:

1. The equilibrium data of H_2S-Sulfolane and H_2S- Propylene Carbonate (PC) systems were successfully correlated using SRK thermodynamic model. The deviation was noticed only for H_2S-Sulfolane system as the temperature increases to 373 ^oK, to give a deviation of less than 5% . Therefore CHEMCAD simulator, with SRK thermodynamic models without modification, is recommended for processes including H_2S- Sulfolane and H_2S- Propylene Carbonate (PC) systems.
2. The thermodynamic models used in present study, PR, and SRK thermodynamic models, used as such without modification, fail to correlate the equilibrium data of H_2S- NMP (N-Methyl-2-Pyrrolidone) system for all temperature range used, and give deviations higher than 20%.
3. Modifications of the thermodynamic models were performed by editing user defined binary interaction parameters (BIP) of the systems used, gives good results.
4. In using CHEMCAD simulator, It must be always resimulate the process with a number of thermodynamic models, or making modifications on a certain model, to verify the suitability of the application.

REFERANCES

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Table(1)Experimental partial pressure–composition data for H_2S-Sulfolane

T ^{o}K	X	P Bar	T ^{o}K	X	P Bar	T ^{o}K	X	P Bar
298.15 Jou et al [4]	0.0206	0.301	323.15 Murrieta et al[3]	0.0267	0.76	373.15 Murrieta et al[3]	0.0383	2.414
	0.1129	1.83		0.059	1.708		0.0676	4.41
	0.19	3.35		0.1166	3.447		0.1155	7.81
	0.299	5.36		0.1999	6.056		0.16	10.913
	0.505	9.99		0.3015	9.58		0.189	13.125
	0.6887	14.3		0.3504	11.427		0.2344	16.546
	0.842	17.6		0.4093	13.757		-	-
	0.9412	19.97		-	-		-	-

Table (2) Experimental partial pressure – composition data for H_2S-NMP

T ^{o}K	X	P Bar	T ^{o}K	X	P Bar	T ^{o}K	X	P Bar
298.15 Murrieta et al[3]	0.2648	2.113	323.15 Murrieta et al[3]	0.1499	1.836	373.15 Murrieta et al[3]	0.0568	1.752
	0.3557	3.323		0.2316	3.243		0.1112	3.681
	0.425	4.489		0.3267	5.305		0.1673	5.869
	0.4853	5.684		0.4192	7.837		0.2255	8.401
	0.538	6.904		0.4992	10.574		0.2778	10.818
	0.5814	8.045		0.5491	12.536		0.3287	13.511
	0.6207	9.174		0.5798	13.848		0.3662	15.586
	0.6539	10.167		-	-		-	-
	0.6812	11.044		-	-		-	-
	0.7057	11.866		-	-		-	-

Table (3) Experimental partial pressure – composition data for H_2S-PC

T ^{o}K	X	P Bar	T ^{o}K	X	P Bar	T ^{o}K	X	P Bar
298.15 Murrieta et al[3]	0.0367	0.817	323.15 Murrieta et al[3]	0.0274	0.965	373.15 Murrieta et al[3]	0.0305	2.331
	0.1147	2.552		0.0665	2.348		0.0609	4.596
	0.1866	4.186		0.1148	4.076		0.1052	8.178
	0.2846	6.524		0.1862	6.843		0.1402	10.915
	0.3668	8.44		0.258	9.671		0.1672	13.104
	0.4418	10.176		0.3102	11.748		0.2041	15.956
	0.5032	11.647		0.3781	14.461		-	-
	0.5573	12.924		-	-		-	-

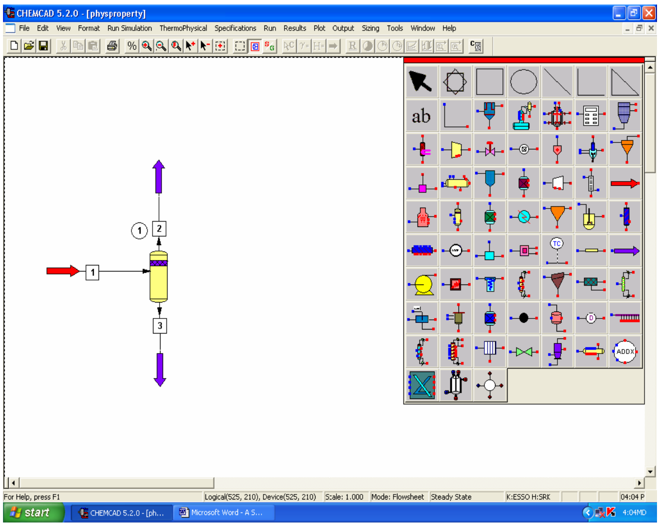

Figure (1) CHEMCAD Simulator Working Window with Main Palette

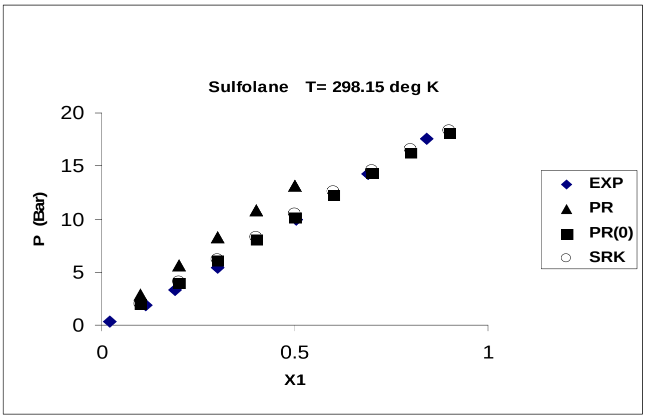

Figure (2) Phase Equilibrium of H_2S-Sulfolane at 298.15 °K

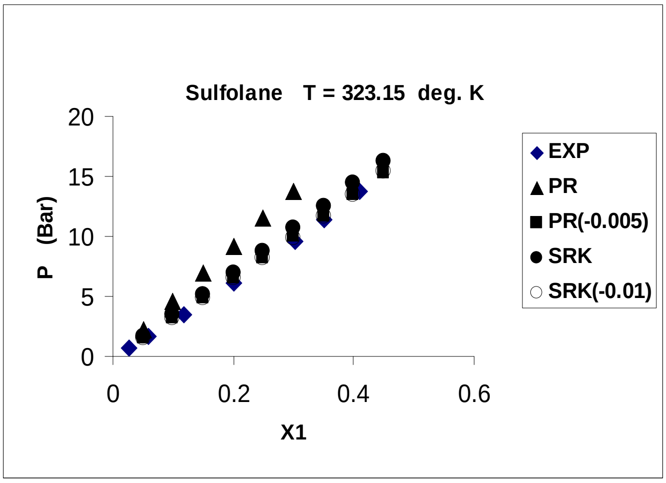

Figure (3) Phase Equilibrium of H_2S-Sulfolane at 323.15 °K

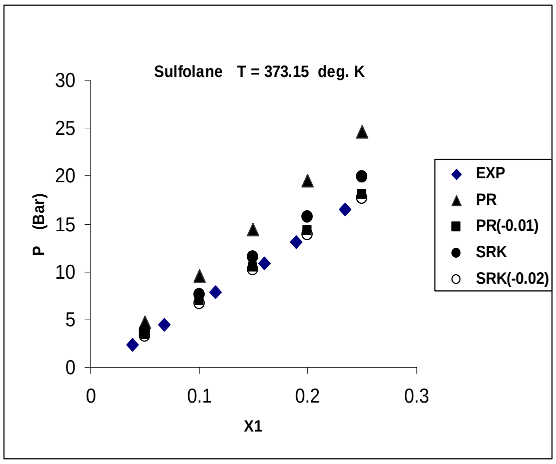

Figure (4) Phase Equilibrium of H_2S-Sulfolane at 373.15 °K

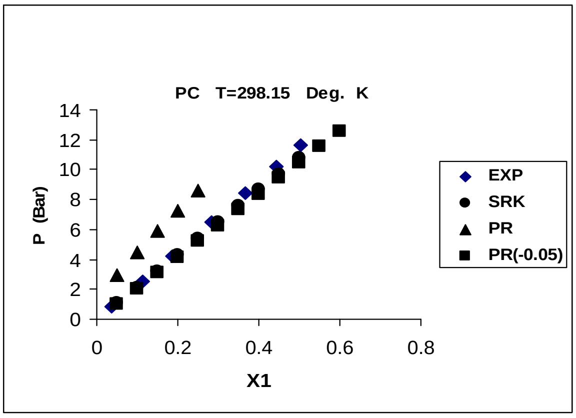

Figure (5) Phase Equilibrium of H_2S-PC at 298.15 °K

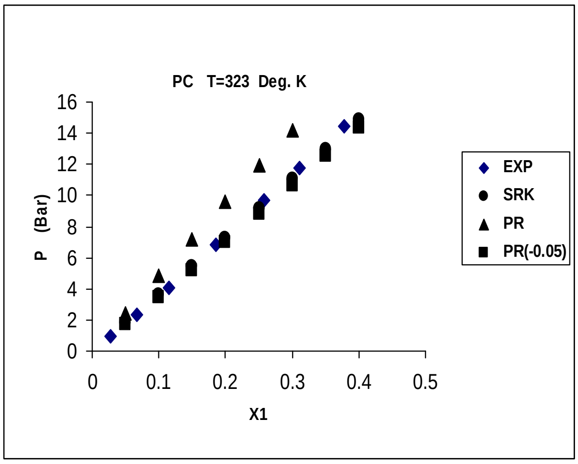

Figure (6) Phase Equilibrium of H_2S-PC at 323.15 °K

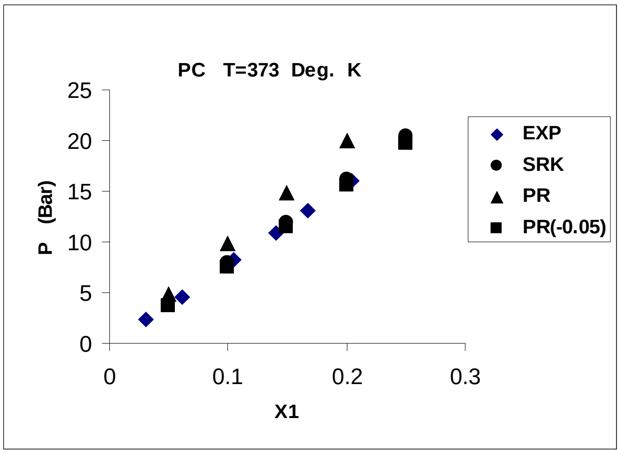

Figure (7) Phase Equilibrium of H_2S-PC at 373.15 °K

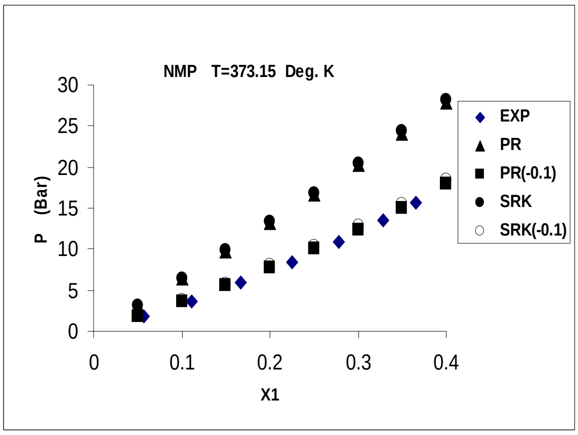

Figure (10) Phase Equilibrium of H_2S-NMP at 373.15 °K

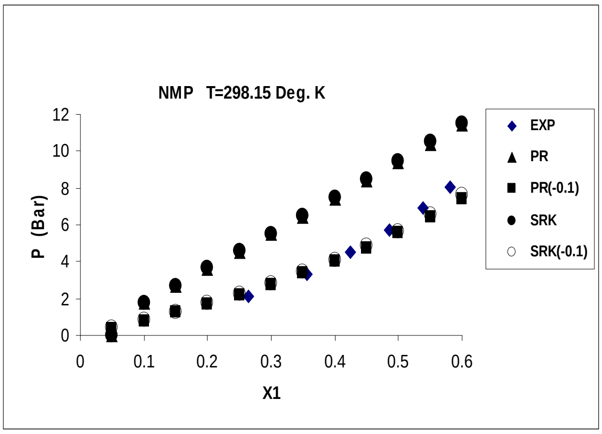

Figure (8) Phase Equilibrium of H_2S-NMP at 298.15 °K

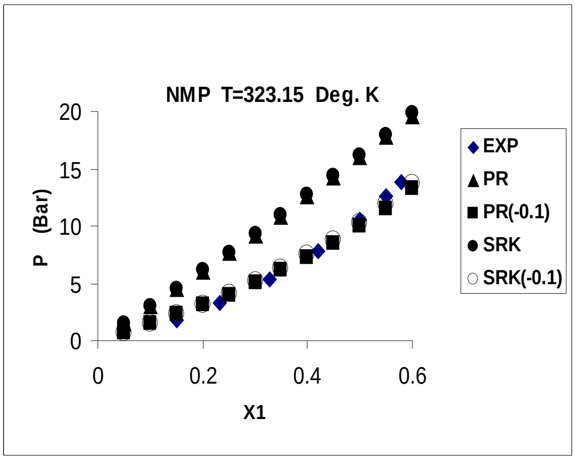

Figure (9) Phase Equilibrium of H_2S-NMP at 323.15 °K

دراسة اتزان الاطوار لغاز كبريتيد الهيدروجين (H_2S) مع عدة مذيبات فيزياوية باستعمال برنامج المحاكاة الجاهز CHEMCAD

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الخلاصة

استعمل برنامج المحاكاة الجاهز CHEMCAD لتحليل معلومات اتزان الأطوار التجريبية، المنشورة في الدوريات العلمية، لغاز كبريتيد الهيدروجين مع عدد من المذيبات الفيزياوية (Sulfolane, Propylene Carbonate (PC), and N-Methyl-Pyrrolidone (NMP)) في درجات حرارة مختلفة (298.15 ^{o}K , 323.15 ^{o}K, and 373.15 ^{o}K) . واستعمل موديلين لديناميك الحرارة (معادلات الحالة) وهما ، (PR, and SRK).

انطبقت بنجاح نتائج برنامج CHEMCAD ولموديل ديناميك الحرارة (SRK) ، مع معلومات اتزان الأطوار التجريبية لغاز H_2S مع المذيبين ((Sulfolane, and Propylene Carbonate (PC))، وبدون أي تحسين للموديلين. بينما لم تنطبق نتائج الموديل (PR).

لم تنطبق نتائج برنامج CHEMCAD لموديلي ديناميك الحرارة (PR and SRK) ،مع معلومات اتزان الأطوار التجريبية للغاز مع المذيب ((N-Methyl-Pyrrolidone (NMP)) وبدون أي تحسين للموديلات، ولجميع درجات الحرارة.

عند تحسين موديلات ديناميك الحرارة بتصحيح قيمة معامل الترابط الثنائي لغاز H_2S والمذيبات الثلاثة اعطت نتائج تطابق جيدة مع معلومات الاتزان التجريبية.

الكلمات الدالة

اتزان الأطوارغاز -سائل برنامج CHEMCAD غاز كبريتيد الهيدروجين ، مذيبات فيزياوية.