



INVESTIGATION OF GAS-LIQUID EQUILIBRIUM OF A SURFACTANT-BASED DESICCANT LIQUID DEVELOPED FOR NATURAL GAS DEHYDRATION

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Abstract. Natural gas is an important source of primary energy that, under normal production conditions, is saturated with water vapor. Water vapor increases the corrosiveness of natural gas, especially when acid gases are present. Several methods can be used to dry natural gas. The objectives of this study were to develop a procedure to absorb the water from natural gas in a new surfactant-based desiccant liquid and to evaluate gas-liquid equilibrium data. The principle of the desiccant liquid preparation is based on microemulsion formation (water-surfactant-oil mixtures). The dynamic method was applied for the determination of the equilibrium data, based on the saturation of the phases. The equilibrium criterion was the constancy in water concentration. Three surfactants were used for the natural gas water removal. The experimental results indicated the feasibility of the water removal from the natural gas using a specially designed absorption column and a desiccant liquid prepared with turpentine and surfactant. The gas-liquid equilibrium data were also calculated by the Peng-Robinson equation of state with the van der Waals and the modified Huron-Vidal mixing rules.

Keywords: natural gas dehydration; gas-liquid equilibrium; Karl-Fischer method; microemulsion; surfactant

1. INTRODUCTION

Thermodynamic properties of natural gas mixtures are important in gas industry, especially in production, processing, storage and transportation (Nasrifar and Bolland, 2006). Natural gas is an important source of energy which, under usual production conditions, is saturated with steam. Its composition is mainly hydrocarbons and some contaminants, and water is one of the most undesirable impurities (Haselden, 1989). Natural gas is treated at the well to remove water, carbon dioxide, sulfur compounds, mercury vapors and higher hydrocarbons (Schmidt et al., 1996). Water represents a critical component because of its conditioning

or processing. Water removal from a natural gas stream reduces the risks of corrosion, formation of hydrates and blockage of ducts (Manning and Thompson, 1991). The solubility of natural gas components, methane and ethane, in pure water has been extensively studied in the past few decades (Wang et al., 2003; Battino, 1982). However, due to their extremely low solubility, the reported data are not in good agreement. The reciprocal is also true, i.e., the solubility of water in natural gas presents low values.

Microemulsions used as reactive absorption media may provide a useful way for enhancing the specific rates of gas absorption taking into account the high solubility that the dispersed

phase may present for the solute gas and the extremely high gas-liquid interfacial area between the oil and water phases (Mehra and Sharma, 1986). Microemulsions refer to thermodynamically stable, transparent mixtures of generally four components, commonly described as surfactant, cosurfactant, oil and an aqueous phase (Mehra and Sharma, 1986). The cosurfactant is a nonionic molecule (typically a short-chain alcohol or amine) that has the function of stabilizing a microemulsified system by decreasing the repulsion forces between the hydrophilic parts of the surfactant molecule (Dantas et al., 2001). When a nonionic surfactant is used in this system, the cosurfactant presence is optional due to the absence of electronic repulsion between the surfactant molecules. In excess of oil, the microemulsion is water-continuous (Winsor I - WI) and in excess of water it is said to be oil-continuous (Winsor II - WII). In Winsor III systems (WIII), three phases are present, where the microemulsion is in equilibrium with both excess aqueous and oil phases, and in Winsor IV (WIV) systems only a microemulsion phase is formed (Paul and Moulik, 1998).

Natural gas dehydration is usually carried out by absorption using a liquid that has affinity for water in counter-flow mode. Among the desiccants liquids used to absorb water from natural gas, one may cite solutions of calcium chloride, lithium chloride and glycol (Manning and Thompson, 1991; Gandhidasan et al., 2001).

In this work, an attempt has been made to develop a new desiccant liquid using surfactants, enabling it to absorb water from natural gas. The absorption of water was evaluated in column experiments, generating gas-liquid equilibrium data and devising a thermodynamic model for the natural gas treatment. It is important to point out the severe conditions established to measure the data, namely low water concentration and high asymmetry of the mixtures, demanding accurate measurements and also advanced equations of state.

2. EXPERIMENTAL

2.1. Chemicals

The chemicals used in the experiments were analytical grade, except turpentine (Petrobras; chemical composition: paraffinic hydrocarbons—min 70%, aromatic hydrocarbons—max 20%, and olefinic hydrocarbons—max 5%; density > 1; viscosity 2.7 cSt at 20°C; distillation range 150–300°C at 760 mmHg), and were used as supplied, without further purification. Surfactants, RDG 60 (98 wt.% of purity) and UNTL L60 (98 wt.% of purity) were supplied by Oxiteno, Brazil, and AMD 60 (98 wt.% of purity) was supplied by PBC, Brazil. The gaseous phase was a mixture of methane (90 vol.%) and ethane (10 vol.%) supplied by AGA and was analytical grade. This synthetic mixture represents the natural gas composition.

2.2. Formulation of the desiccant liquid

The desiccant liquid is formed by turpentine (organic phase), distilled water (aqueous phase) and commercial surfactants (RDG 60, UNTL L60 and/or AMD 60). The RDG 60 surfactant is derived from the reaction of nonylphenol with ethylene oxide. The UNTL L60 surfactant is derived from the reaction of lauryl alcohol of natural origin with ethylene oxide. The structures of these surfactants, together with the probable structure of the AMD 60 surfactant (diethanolamide of coconut fatty acids) are shown in Figure 1.

To obtain the desiccant liquid, it was first necessary to determine the extent of the microemulsion region in a ternary phase diagram. The regions inside the phase diagram

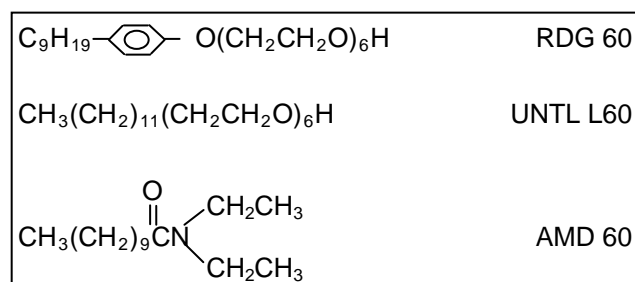


Figure 1. Chemical structures of the RDG 60, UNTL L60 and AMD 60 nonionic surfactants.

were described as miscible (microemulsion) and immiscible. The solubility curve for the water + turpentine + surfactant ternary system was determined by the cloud-point method (Ince and Kirbaslar, 2002). Binary mixtures of known compositions were shaken in a glass stopped cell equipped with a magnetic stirrer and jacketed for circulating water from a constant temperature bath at 305.15 ± 0.02 K. The third component was progressively added until the cloud-point transition was reached. The end point was determined by observing the transition from a homogenous to a heterogeneous mixture.

2.3. Experimental apparatus, instruments and analytical methods

The equilibrium measurements were carried out in an apparatus consisting of a gas humidification system and an absorption column (Figure 2). In this apparatus, the solubility of the water, present in the gas phase, in the desiccant liquid was determined. The maximum working pressure was 0.40 MPa and the operating temperature was 301.15 K.

The humidification system follows the procedure described in ASTM D 4178/82, revised in 1999 (ASTM D-5454/93, ASTM D-4178/82). It involves the calibration of the humidity analyzers, based on standard quantities of water (Cavalcanti Neto et al., 2002). In order to saturate the gas and control its water concentration, two adsorption vases have been developed. In the first one, filled with dried molecular sieve, the complete dehydration of the gas is made. In the second one, filled with water-saturated molecular

sieve, the controlled humidification occurs. The desired water content in the gas is obtained by properly adjusting the valves that feed the column, knowing the temperature and therefore the corresponding water vapor pressure.

The column is equipped with a gas disperser at the base. This device aims to homogenize the gas flow in the liquid column either longitudinally and radially. It also increases the interfacial area.

The water concentration in the gas and liquid phases has been monitored and measured by the Karl Fischer method (Mettler Toledo-DL 39). This method is based on the oxidation of SO_2 by I_2 in the presence of water, which is quite sensitive. For the gas phase, a procedure was developed whereby the sample is injected into the analyzer at a 200 mL/min flowrate during 30 seconds. For the liquid phase the standard methodology was used. The Karl Fischer method was chosen due to its high sensitivity, which is a requirement of the experiment, as the water concentrations are quite low. The reproducibility of the water concentrations analysis with these procedures is estimated to be ± 10 ppm.

2.4. Experimental procedure

The dynamic method has been used to obtain the gas-liquid equilibrium data. The principle of this method consists in passing the gas phase into the bulk of the liquid phase fixed at a relatively low flowrate (Grenner et al., 2005). The duration of the flow of the gas phase is the time to reach the steady-state, which is considered as an equilibrium condition in the experimental setup. The steady-state is

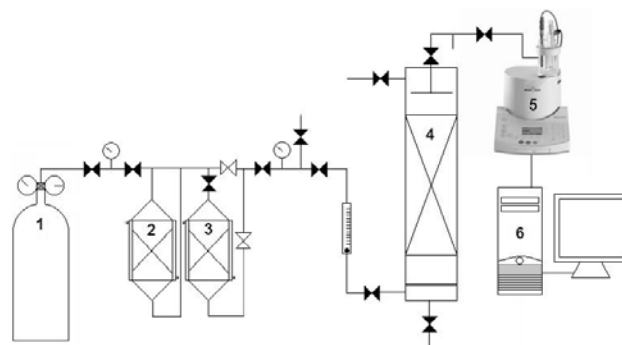


Figure 2. Schematics of the experimental apparatus: (1) natural gas bottle, (2) dehydration vase, (3) humidification vase, (4) absorption column, (5) Karl Fischer analyzer, and (6) Computer for data acquisition.

monitored by the constancy of the gas phase water concentration.

The first procedure is to let the gas pass through all the lines for cleaning purposes, i.e., in order to remove any residual humidity present in the ducts, at a 200 mL/min flowrate. Then measurements of the humidity of the gas are performed in order to determine the initial water concentration in the gas. The second step is the injection of the desiccant liquid in the absorption column. This operation is carried out with the aid of a volumetric pump. The volume of the liquid phase into the cell has been fixed for all experiments i.e., 500 mL. From this moment the experiment is started by allowing the gas to flow through the liquid and the outlet gas concentration is monitored with time to determine the equilibrium point, or constancy.

2.5. Thermodynamic modeling

The thermodynamic modeling of the phase equilibrium data was performed with the Peng-Robinson equation of state (Peng and Robinson, 1976). The classical and MHV2 mixing rules have been used in a Flash mode of calculation (Dahl, 1991; Sandler, 1989). The critical properties for the surfactants RDG 60, UNTL L60 and AMD 60 were estimated by the Lydersen method, which is also a group contribution method (Reid et al., 1987). Alpha parameters for the pure components have been

calculated using the expansion of Mathias and Copeman, with estimated parameters based on vapor pressure data (Chiavone-Filho et al., 2001). The parameters have been used with the MHV2 mixing rules. Table 1 presents the required pure component parameters used in the Peng-Robinson equation of state.

3. RESULTS AND DISCUSSION

3.1. Formulation of the desiccant liquid

In order to identify the miscible regions, four ternary phase diagrams were constructed (Figure 3), for the mixtures with turpentine, water and surfactant (RDG 60, RDG60/AMD 60, UNTL L 60 and UNTL L 60/AMD 60). Table 2 shows the hydrophilic-lipophilic balance (HBL) of the studied surfactants and mixtures.

The mass ratio applied to RDG 60/AMD 60 and UNTL L60/AMD 60 have been fixed to 1:1. The determination of the diagrams was performed by titrating water onto the organic phase, with prefixed ratios of surfactants. By doing this, the phase boundaries were obtained.

In Figure 3, it can be verified that the miscible region is present in all systems (in the surfactant/oil side of the ternary diagram). This is a fundamental condition for the desiccant formulation. It is also possible to verify that the addition of AMD 60 to the system (containing

Table 1. Pure component parameters^a used in the thermodynamic modeling.

Compound \ Parameter ^a	T_c / K	P_c / bar	ω	z_c	C_1	C_2	C_3
Methane ^b	190.58	45.44	0.0108	0.2880	0.5741	-0.4501	0.6338
Ethane ^b	305.42	48.16	0.0990	0.2840	0.6968	-0.3094	0.4073
Decane (Turpentine) ^b	618.45	20.95	0.4842	0.2490	1.1778	0.5121	-1.2714
Water ^b	647.30	217.60	0.3440	0.2330	1.1221	-0.7092	0.7179
RDG 60 ^c	743.15	8.63	0.5348	0.1189	0	0	0
UNTL L60 ^c	872.79	8.01	0.6486	0.1652	0	0	0
AMD 60 ^c	775.35	7.90	0.4077	0.1103	0	0	0

^a T_c is the critical temperature; P_c is the critical pressure; ω is the acentric factor; Z_c is the critical compressibility factor; and C_1 , C_2 , C_3 are the Mathias and Coperman alpha parameters.

^b Reported values. ^c Calculated values.

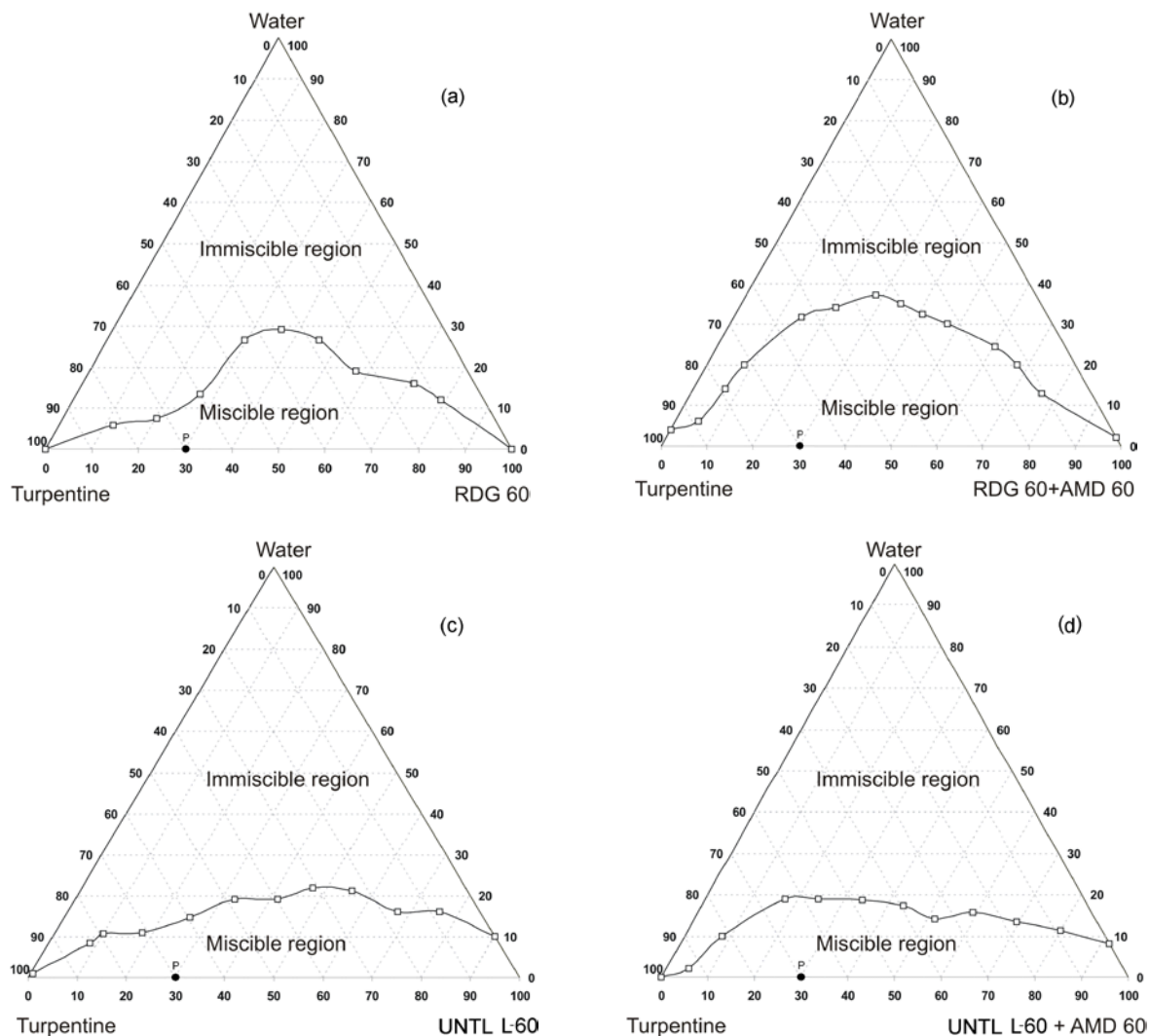


Figure 3. Ternary phase diagrams showing the miscible regions at 305.15K, for the systems with turpentine, water and (a) RDG 60, (b) RDG 60-AMD 60, (c) UNTL L60, and (d) UNTL L60-AMD 60.

RDG60) provokes an increase in the extent of the miscible region. This is due to the fact that AMD 60 allows, at the same time, the formation of water-in-oil and oil-in-water miscible regions (bicontinuous system). AMD 60 can not be used alone as surfactant in the formulation of the desiccant fluid because the

miscible region is not formed. The HBL of all used surfactants indicates that they promote the formation of systems in the boundary area between water-in-oil and oil-in-water systems (Table 3).

For the formulation of the desiccant liquids, a volumetric proportion of 30% surfactant and 70% turpentine was fixed. This concentration corresponds to the miscible region on the binary mixture, see point P in Figure 3.

Table 2. Hydrophilic-lipophilic balance (HBL) of surfactants and mixtures.

Surfactant	HBL
RDG 60	10.9
AMD 60	11.0
UNTL L60	11.5
RDG 60/AMD 60	10.95
UNTL L60/AMD 60	11.25

3.2. Phase equilibrium data

The water solubility presented in the mixture of methane and ethane in the liquid phase containing the five studied desiccant fluids (RDG 60-Turpentine, RDG 60/AMD 60-Turpentine, UNTL L60-Turpentine, and UNTL L60/AMD 60-Turpentine) were determined at

Table 3. Properties of surfactants according to its HLB Values.

HLB	Property	HLB	Property
4-8	Antifoaming agent	12-15	Oil-in Water emulsifier
7-11	Water-in-oil emulsifier	16-20	Stabilizer

305.15K and 0.40MPa. The experimental data are presented in Table 4 and Figures 4 and 5.

Figures 4 and 5 show the y-x diagrams for the five studied systems. The same ordinate has been fixed for all diagrams in order to evaluate the dehydration capability. It may be observed that the new desiccant liquid based on turpentine and surfactant presented a satisfactory behavior as dehydrating agent.

The addition of the AMD 60 has successfully increased the dehydration capability. Therefore the new desiccant liquids, formulated with a reduced amount of surfactants, when compared to the commonly used triethylene glycol, may be useful for dehydration of natural gas, with lower costs. Furthermore, these liquids present other attractive advantages such as stability and flexibility in terms of the amount of water that can be absorbed, as the limits of miscibility have demonstrated. Another interesting aspect is the possibility to recycle the desiccant liquid via simple water evaporation by heating.

A thermodynamic model with equation of state (EoS) has also been provided for the studied systems. The MHV2 mixing rule with the UNIFAC model provided a better representation, but only fairly. This is due to the fact that group contribution methods like

UNIFAC do not consider surfactant molecules in the data basis. These molecules present two completely different groups at each end.

4. CONCLUSIONS

The formulated desiccant liquids using turpentine and nonionic surfactants proved to be applicable in the dehydration of natural gas by absorption.

The dynamic method together with the accuracy of the Karl-Fisher analyzer was properly used for the determination of the gas-liquid equilibrium data even at low water concentration.

The gas-liquid equilibrium curves have also been described in terms of water concentration using the Peng-Robinson equation of state in its original form and also with the MHV2 mixing rule using UNIFAC contribution method. Particularly the system with RDG 60 could be satisfactorily represented with the PR-MHV2 model.

The results indicate that the desiccant liquid with RDG 60 and Turpentine presented better water gas-liquid absorption effects. This may be explained by the relatively high water affinity of the RDG 60 which can also be seen

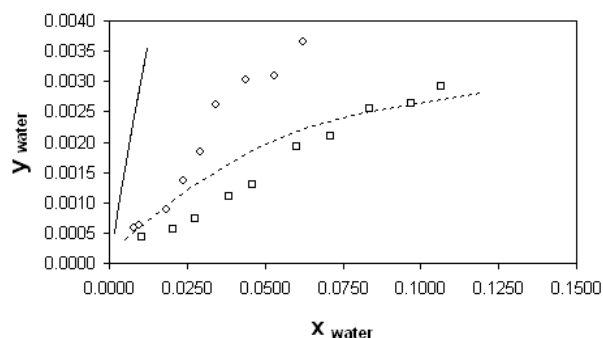


Figure 4. Water gas-liquid equilibrium data for the systems Water-RDG 60-Turpentine-Methane-Ethane (○ experimental and ---- Peng-Robison/MHV2); Water-RDG 60-AMD 60-Turpentine-Methane-Ethane (□ experimental and — Peng-Robison/MHV2), at 305.15 K and 0.40 MPa.

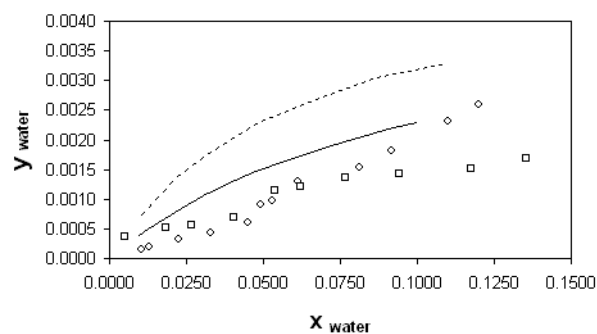


Figure 5. Water gas-liquid equilibrium data for the systems Water-UNTLL 60-Turpentine-Methane-Ethane (○ experimental and ---- Peng-Robison/MHV2); Water-UNTLL 60-AMD 60-Turpentine-Methane-Ethane (□ experimental and — Peng-Robison/MHV2), at 305.15 K and 0.40 MPa.

Table 4. Water gas-liquid equilibrium data at 305.15 K and 0.40 MPa.

SYSTEM	MOLE FRACTION	VALUES									
Water-RDG 60-Turpentine-Methane-Ethane	x_{water}	0.00776	0.00978	0.01824	0.02385	0.02940	0.03430	0.04399	0.05311	0.06835	0.06245
	y_{water}	0.00059	0.00063	0.00088	0.00136	0.00185	0.00261	0.00303	0.00309	0.00418	0.00365
Water-RDG 60-AMD 60-Turpentine-Methane-Ethane	x_{water}	0.01060	0.02057	0.02771	0.03828	0.04614	0.06002	0.07087	0.08339	0.09688	0.10674
	y_{water}	0.00044	0.00057	0.00074	0.00110	0.00131	0.00193	0.00210	0.00255	0.00264	0.00291
Water-UNTL L60-Turpentine-Methane-Ethane	x_{water}	0.01044	0.01308	0.02258	0.03275	0.04502	0.04932	0.05280	0.06137	0.08107	0.09177
	y_{water}	0.00015	0.00019	0.00032	0.00044	0.00060	0.00090	0.00097	0.00131	0.00154	0.00181
Water-UNTL L60-AMD 60-Turpentine-Methane-Ethane	x_{water}	0.00497	0.01838	0.02674	0.04046	0.05383	0.06194	0.07681	0.09437	0.11753	0.13538
	y_{water}	0.00038	0.00052	0.00056	0.00070	0.00115	0.00121	0.00135	0.00142	0.00151	0.00170

x_{water} – mole fraction of the liquid phase

y_{water} – mole fraction the gaseous phase

by the phase boundary of the ternary liquid diagrams.

ACKNOWLEDGEMENTS

The authors acknowledge financial support from ANP – Brazilian National Agency of Petroleum, Natural Gas and Biofuels.

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