# High-Pressure Solubility of Methane (CH$_4$) and Ethane (C$_2$H$_6$) in Mixed Polyethylene Glycol Dimethyl Ethers (Genosorb 1753) and Its Selectivity in Natural Gas Sweetening Operations

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ABSTRACT: The solubility of methane (CH$_4$) and ethane (C$_2$H$_6$) in a mixture of polyethylene glycol dimethyl ethers (Genosorb 1753) was measured at (298.15, 313.15, and 333.15) K and at pressures up to 7700 kPa using a Jerguson equilibrium cell. The solubility data of CO$_2$ and light hydrocarbons (CH$_4$ and C$_2$H$_6$) in Genosorb 1753 were compared with the solubility in other physical solvents. The results were correlated with the Peng−Robinson equation of state (PR-EOS), and the interaction parameters are reported. Among the activity coefficient models, the Non-Random Two Liquid Theory (NRTL) model fitted the data well with an absolute average deviation of 6 %. Henry's Law constants (H_{CH_4} and $H_{C_2H_6}$) and the excess properties (excess Gibbs free energy (G^E), excess entropy (S^E), and excess enthalpy (H^E)) of the liquid mixture were predicted at each temperature using the NRTL activity coefficient model over the full range of composition. The enthalpy of solution and the partial molar enthalpy of mixing for all gases were determined at infinite dilution. In addition, the enthalpies of solution for all the gases were calculated using the Clausius−Clapeyron equation. The coabsorption of hydrocarbons (CH$_4$ and C$_2$H$_6$) with CO$_2$ (selectivity) was evaluated with the following function $\{H_{CO_2}/(H_{CH_4} \cdot H_{C_2H_6})\}$. Compared to other solvents used in gas sweetening, Genosorb 1753 was found to have the highest absorption capacity for CO$_2$ and a low capacity for CH$_4$ but a higher capacity for C$_2$H$_6$.
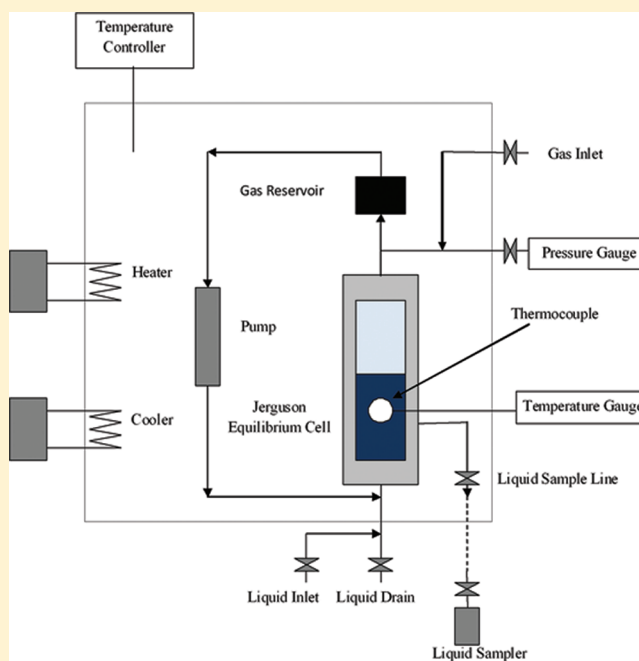
INTRODUCTION

From both theoretical and practical points of view, it is of great need to study the solubility of gaseous solutes in solvents. The removal of acid gases such as CO$_2$, H$_2$S, and COS from gas streams is a very essential operation for petrochemical, oil refineries, ammonia manufacture, coal gasification, and natural gas purification plants.[1] The removal process mainly involves the absorption of the acid gas into solvents at low temperature followed by a subsequent stripping of the acid gas from the solvent at high temperature. The solvents used for the removal of these acid gases are classified as chemical, physical, or hybrid (physical + chemical) solvents.[2] The absorption capacity of a chemical solvent depends on the stochiometry of the reaction, whereas for a physical solvent it is function of the partial pressures of the dissolved gases. The heats of absorption and desorption are smaller for the physical solvents compared to the chemical solvents due to the lack of formation of any chemical species. This makes the use of physical solvents cost-effective by savings in the heat to regenerate the solvent, but these savings are offset by the

high cost of taller absorbers or the increased liquid circulation rate required to maintain the same purification target.[3]

During the design of the absorption/stripping sections, accurate information regarding the vapor−liquid equilibrium (VLE), the physicochemical and thermodynamic properties, the kinetics, the mass transfer, and the chemical reaction equilibrium of these solvents is required.[4] The shape of the VLE (solubility) curve determines the height of the absorption towers. The curve for physical absorption is linear up to relatively high partial pressures of acid gases, whereas the strong interactions between an acid gas and a chemical solvent result in a nonlinear solubility profile. This results in the requirement to have more theoretical stages for a physical solvent compared to a chemical solvent.[1] Additionally, with an existing gas-purification setup, a solvent with an enhanced gas solubility can

be retrofitted to allow plant operation at a lower solvent circulation rate, leading to substantial energy savings.[3] Physical solvents are most suited for high-pressure bulk removal applications. A good physical solvent should have a high capacity for acid gas absorption, a low capacity for hydrocarbon absorption (selectivity), a high boiling point, and a low freezing point, be easily regenerated, have both thermal and chemical stabilities, have a low corrosivity, have a low to moderate viscosity, and finally be available and inexpensive. Some of the listed properties are at least contradictory, and compromises are unavoidable. Most of the solubility data are proprietary in nature and are not available in the open literature.

Zawacki et al.[5] screened more than 100 solvents and concluded that n-formyl morpholine (NFM) and tetraethylene glycol dimethyl ether (TTEGDME) are the most promising solvents. Sciamanna and Lynn[6] measured the solubility of CO_2, H_2S, propane, and n-butane in five glycol ethers (diethylene glycol dimethyl ether (DEGDME), triethylene glycol dimethyl ether (TEGDME), tetraethylene glycol dimethyl ether (TTEGDME), diethylene glycol monomethyl ether (DEGMME), and triethylene glycol monobutyl ether (TEGMBE)) with an automated gas solubility measurement and reported the results in the form of Henry's Law constants at infinite dilution at 298.15 K. Some solubility data of CO_2 in glycol ethers from several sources were collected by Fogg[7] and published in the IUPAC solubility data series. Sweeney et al.[3] published the solubility of CO_2 in DEGDME, TEGDME, and TTEGDME at 298.15 K. Porter et al.[8] reported the solubility of CO_2 in polyethylene glycol dimethyl ethers (Selexol) at 298.15 K. Gainar et al.[9] measured the solubility of CO_2, N_2, and H_2 in a mixture of dimethyl ether polyethylene glycols at high pressures. In a preliminary literature study, Henni and Mather[10] concluded that ethylene glycol ethers were the solvents with the highest potential for gas sweetening considering the solubility of acid gases CO_2, CH_4, and C_2H_6 in 34 physical solvents. The solubility of CO_2 in 14 polyethylene glycol ethers including ethylene glycol monomethyl ether (EGMME), DEGMME, triethylene glycol monomethyl ether (TEGMME), ethylene glycol dimethyl ether (EGDME), DEGDME, TEGDME, TTEGDME, diethylene glycol monoethyl ethers (DEGMEE), diethylene glycol diethyl ethers (DEGDEE), ethylene glycol monobutyl ether (EGMBE), diethylene glycol monobutyl ether (DEGMBE), triethylene glycol monobutyl ether (TEGMBE), polyethylene glycol dimethyl ether (PEGDME 250), NFM, and sulfolane (TMS) was reported by Henni et al.[11] in the form of Henry's Law constants. Henni et al.[12] also reported the solubility of CH_4 and C_2H_6 in the best five glycol ethers (DEGDME, TEGDME, TTEGDME, TEGMBE, PEGDME 250) in terms of capacity for CO_2 absorption. The selectivity was represented in the form of a function of Henry's Law constants of the gases: $[H_{CO_2}/(H_{CH_4}\cdot H_{C_2H_6})]]$ for natural gas sweetening operations and compared to other promising physical solvents (NFM, n-methyl pyrrolidinone (NMP), and sulfolane).

TEGDME and TTEGDME are two of a number of dimethyl glycol ethers that make Selexol (a mixture of polyethylene glycol dimethyl ethers), a popular physical solvent. It is used as a physical absorption medium in acid gas removal and waste air treating processes and to clean synthesis gases (Kohl and Riesenfeld,[13] Astarita et al.,[2] and Clare and Valentine[14]). The mixture is characterized by a low vapor pressure, miscibility with water, and high viscosity. It has a low enthalpy of vaporization which results in a low desorption energy consumption. The absorptive capacity of Selexol is high for hydrogen sulfide (H_2S), mercaptans (R-SH), and other sulfur-containing compounds (CS_2, COS) (Schmidt et al.[15]). Being a physical solvent, Selexol

needs very little energy for its regeneration. Because of small losses in vaporization, low foaming, and degradation, a mixture of polyethylene glycol dimethyl ethers is considered as, environmentally, less toxic compared to other solvents (Clare and Valentine[14]). It has a lubricity which leads to solid-free solvent and results in a reduced level of maintenance in operations (Woelfer[16]). Selexol is used in over 60 gas treating plants as a solvent for Integrated Gasification Combined Cycle (IGCC) synthesis gases. The present work was undertaken to provide data for Genosorb 1753 (mixed polyethylene glycol dimethyl ethers) at elevated pressures and at different temperatures. These data can be used in equations of state for the prediction of multicomponent vapor—liquid equilibrium.

The solubility of CO_2 in Selexol was measured by Porter and Eck[17] at low pressures, as reported by Macchietto et al.[18] Xu[19] used low-pressure data at different pressures and temperatures to measure the solubilities of CO_2 in Selexol and reported the data in the form of Henry's Law constants. The Selexol process, was patented by Allied Chemical Corporation in the late 1960s and later purchased by Norton in 1982. Union Carbide bought it in 1990, and it was finally acquired by Dow Chemical Co. in 2001.[12] The absorption liquid used in the Selexol process is similar to Genosorb 1753 (i.e., a mixture of polyethylene glycol dimethyl ethers $[CH_3O(CH_2CH_2O)_nCH_3]$ with n, for Genosorb 1753, mainly between 4 and 10, and between 3 and 11 for dimethyl ethers of polyethylene glycol (Schmidt and Mather[15]). The physical properties of Genosorb 1753 were reported by Li et al.[20] In a recent work,[21] we have reported some high partial pressure solubility data of CO_2 in Genosorb 1753 at (298.15, 313.15, 323.15, and 333.15) K. In this work, we are reporting high-pressure solubility data of CH_4 and C_2H_6 along with their selectivity $[H_{CO2}/(H_{CH_4}\cdot H_{C_2H_6})]$ at (298.15, 313.15, and 333.15) K in the same solvent. The solubility of CH_4 and C_2H_6 in Genosorb 1753 is important for the economical assessment of natural gas operations. All data were correlated with the Peng—Robinson equation of state (PR-EOS) model and activity coefficient models (WILSON,[22] VANLAAR,[23] and NRTL[24]).

■ EXPERIMENTAL SECTION

The experimental setup used in this work (Figure 1) is similar to that employed by Kadiwala et al.[25] This setup consists of a high-pressure Jerguson cell with design pressure of 34 500 kPa and a magnetic pump with a working pressure of 82 700 kPa and a capability of bubbling $(100\cdot10^{-6})$ $m^3\cdot min^{-1}$ of vapor through the liquid phase. The total volume of the cell is about $(250\cdot10^{-6})$ m^3. An air bath (Z16, Cincinnati, OH) was used to maintain the constant temperature for the entire experimental setup. The temperature of the equilibrium cell was held within ± 0.1 K. A digital temperature indicator purchased from Omega (DP97) was employed to measure the temperature, and the pressure inside the cell was measured with a Heise pressure gauge with ± 0.1 % accuracy for the full range of (0 to 68948) kPa. The cell was cleaned and loaded with solvent (Genosorb 1753) using the procedure described in Kadiwala et al.[25] and Henni and Mather.[26,27] The liquid solvent within the cell was permitted to reach thermal equilibrium, and then pure gas (CH_4 and C_2H_6) was introduced from the top of the cell through a needle valve until the preferred pressure was reached. The magnetic pump controlled the circulation of the gas and its dispersion in small bubbles into the liquid solvent. The experiment was run for at least 8 h until thermodynamic equilibrium conditions were reached (constant pressure for more than half an hour). A liquid phase sample was drawn from the side of the cell into a
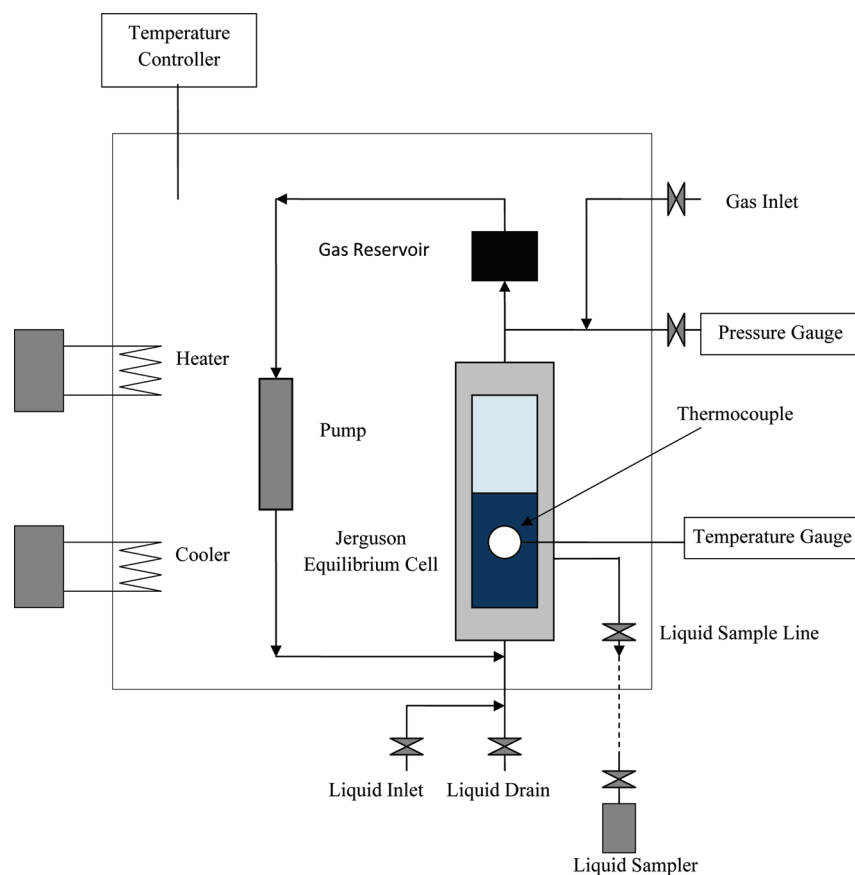
Figure 1. Vapor—liquid equilibrium experimental setup.

$(40 \cdot 10^{-6})$ m^3 sampling bomb. The bomb was weighed before and after the sample collection to obtain the mass of the sample. Then, the bomb was attached to a $(50 \cdot 10^{-6})$ m^3 buret with a magnetic stirring bar inserted inside to assist the degassing process. Slowly, the valve was opened and closed until all the gas evolved from the liquid sample and collected over a buret with mercury. The mass of gas evolved was calculated using atmospheric pressure, room temperature, and the volume collected. The residual gas at atmospheric pressure was measured by chromatography and was found to be negligible. A gas chromatograph (6890N) from Agilent was used to analyze the liquid sample. The GC 6890N was equipped with an (Agilent) HP-Plot Q (30 m long, $(0.53 \cdot 10^{-3})$ m I.D. and $(40 \cdot 10^{-6})$ m thick) capillary column, an automatic injector (7683 series), and a Thermal Conductivity Detector (TCD). The oven was kept at a constant temperature of 523.15 K and programmed to reach 553.15 K until all the compounds in Genosorb 1753 were eluted. The detector temperature was set to 563.15 K. Helium was used as a carrier gas with a flow rate of $(7 \cdot 10^{-6})$ m$^3 \cdot$min^{-1}. Genosorb 1753 was obtained from Clariant International Ltd. (GmbH, Frankfurt am Main, Germany) and was used without further purification. Methane (CH$_4$) and ethane (C$_2$H$_6$) were purchased from Praxair with instrumental grade having purity >99 mass %. The uncertainty in the solubility experiment was estimated to be within ± 2 % by comparing the solubility data of CO$_2$ in methanol.[28]

■ RESULTS AND DISCUSSION

Solubility Data and Modeling. Data for the solubilities of methane (CH$_4$) and ethane (C$_2$H$_6$) in Genosorb 1753 were obtained at (298.15, 313.15, and 333.15) K at pressures up to

approximately 7600 kPa. The results are presented in Tables 1 and 2. The solubility data at (298.15, 313.15, and 333.15) K were correlated using the PR-EOS model and activity coefficient models. Henni et al.[26] studied the solubility of CO$_2$ in TEGMME (triethylene glycol monomethyl ether), the lightest component in Genesorb 1753, and reported that no TEGMME was detected in the vapor phase even at 373.15 K. On the basis of the values of the vapor pressures and the study of the lightest component of the mixture, it was assumed that there will be negligible amounts of Genosorb 1753 in the vapor phase. An intelligent gravimetric microbalance (IGA-003) was used to measure the vapor pressure of Genosorb 1753 and reported in our previous work.[21]

The value of n in the polymer Genosorb 1753 [CH$_3$O(CH$_2$CH$_2$O)$_n$CH$_3$] was estimated using the molecular weight [number average molecular weight (M_n = 339.9)] obtained from electrospray low-resolution ion-spectroscopy analysis (University of Alberta, Chemistry Department). The critical pressure and temperature for Genosorb 1753 were estimated using the Klincewicz—Reid equation.[29] The acentric factor was obtained from the Lee—Kesler correlation.[30] The calculated parameters for pure Genosorb 1753 are presented in Table 3. The parameters for pure CO$_2$,[31] CH$_4$, and C$_2$H$_6$ were taken from Daubert and Danner.[32] The vapor pressure data of Genosorb 1753,[21] CH$_4$,[33] and C$_2$H$_6$[34] were regressed using an extended Antoine equation in Aspen plus DRS (Data Regression System). The coefficients of the extended Antoine equation are given in Table 4. The optimum interaction parameter, δ_{12}, in the mixing rule of the equation of state was obtained by minimizing the error in the predicted bubble point pressure. The

Table 1. Solubility of CH$_4$ in Genosorb 1753

298.15 K			313.15 K			333.15 K		
P_{CH_4}/kPa	x_{CH_4}	γ_{CH_4}	P_{CH_4}/kPa	x_{CH_4}	γ_{CH_4}	P_{CH_4}/kPa	x_{CH_4}	γ_{CH_4}
7210.7	0.134	0.06	7406.3	0.140	0.05	6730.6	0.135	0.03
6898.8	0.131	0.06	6375.2	0.124	0.04	6230.7	0.129	0.03
6804.5	0.131	0.06	5326.1	0.119	0.04	5981.4	0.123	0.03
6393.0	0.125	0.06	4328.4	0.102	0.04	5713.1	0.120	0.03
5345.8	0.113	0.06	4147.5	0.090	0.03	5453.6	0.115	0.03
4895.5	0.106	0.05	3996.9	0.086	0.03	5096.6	0.112	0.03
4422.2	0.099	0.05	3464.7	0.082	0.03	4712.1	0.106	0.03
4237.2	0.100	0.05	3396.7	0.080	0.03	4369.7	0.104	0.02
3929.6	0.094	0.05	3061.2	0.073	0.03	3416.3	0.090	0.02
3380.8	0.085	0.05	2266.3	0.065	0.03	2674.8	0.076	0.02
2773.9	0.074	0.04	2135.7	0.057	0.03	2458.6	0.075	0.02
1625.3	0.052	0.04	1674.7	0.047	0.02	1697.9	0.056	0.02
1098.8	0.039	0.03	1615.9	0.041	0.02	1265.2	0.047	0.02
697.4	0.028	0.03	1112.6	0.038	0.02	1129.9	0.046	0.02
638.6	0.027	0.03	1069.1	0.039	0.02	705.8	0.031	0.01
509.7	0.020	0.03	644.8	0.024	0.02	378.9	0.020	0.01
383.4	0.018	0.03	641.9	0.032	0.02	238.8	0.013	0.01
314.9	0.016	0.03	403.3	0.014	0.02	186.8	0.014	0.01
185.5	0.013	0.03	378.6	0.022	0.02			
			205.8	0.011	0.02			
			169.4	0.013	0.02			
			141.8	0.011	0.02			

Table 2. Solubility of C$_2$H$_6$ in Genosorb 1753

298.15 K			313.15 K			333.15 K		
$P_{C_2H_6}$	$x_{C_2H_6}$	$\gamma_{C_2H_6}$	$P_{C_2H_6}$	$x_{C_2H_6}$	$\gamma_{C_2H_6}$	$P_{C_2H_6}$	$x_{C_2H_6}$	$\gamma_{C_2H_6}$
6358.9	0.470	0.60	6628.0	0.451	0.55	7655.12	0.481	0.54
4310.8	0.460	0.59	5863.5	0.450	0.55	7154.34	0.454	0.50
4292.3	0.450	0.58	5539.6	0.455	0.55	7096.65	0.444	0.49
4187.3	0.450	0.58	4847.0	0.434	0.52	6851.73	0.433	0.48
3653.3	0.420	0.55	4319.7	0.396	0.49	6585.44	0.432	0.48
3439.4	0.400	0.53	3516.7	0.353	0.44	6247.38	0.419	0.47
2833.8	0.340	0.47	3110.1	0.312	0.40	5921.38	0.399	0.45
2322.9	0.300	0.43	2716.7	0.284	0.37	5465.86	0.399	0.45
2127.3	0.280	0.42	1801.8	0.209	0.31	4973	0.374	0.42
1815.1	0.250	0.39	1209.9	0.161	0.28	4553.03	0.353	0.40
1343.1	0.200	0.35	738.9	0.125	0.25	4177.79	0.340	0.39
939.4	0.160	0.32	376.9	0.085	0.23	3843.81	0.318	0.37
771.7	0.150	0.31	258.9	0.063	0.21	3308.95	0.304	0.35
565.4	0.130	0.29	194.0	0.056	0.21	2907.1	0.254	0.30
411.5	0.120	0.29				2395.01	0.233	0.29
283.8	0.090	0.27				1969.92	0.195	0.26
220.7	0.080	0.26				1510.9	0.159	0.24
170.0	0.070	0.25				1131.31	0.136	0.22
						791.01	0.105	0.20
						386.95	0.070	0.18
						173.09	0.051	0.17

following absolute average deviation calculation was used

$$AAD\ \% = \frac{\sum\left[abs\left(\dfrac{exp - calc}{exp}\right)\right]}{NP} \cdot 100\ \% \qquad (1)$$

where exp and calc are the experimental and calculated values (partial pressures) of the gas, and NP is the number of experimental data points. The optimized interaction parameters

of PR-EOS for CH$_4$ and C$_2$H$_6$ in Genosorb 1752 are listed in Table 5. The PR-EOS combined with the original van der Waals mixing rules did not correlate the data very well for these systems. The Peng−Robinson equation of state correlated the data with objective functions of 13.6 % for CH$_4$ and 7.2 % for C$_2$H$_6$. This may be because the original PR-EOS is best suited for nonpolar or mildly polar mixtures.[10] Consequently, few activity coefficient models were used to correlate the solubility data and obtain the interaction parameters.

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Table 3. Pure Component Parameters

components	mol. wt.	T_B K	T_c K	P_c kPa	ω
Genosorb[21]	339.9	523.15	626.6	5335.6	2.416
CO_2[31]	44.01	82	304.2	7381	0.225
CH_4[32]	16.01	111.7	109.6	4604.3	0.011
C_2H_6[32]	30.07	184.5	305.4	4880.1	0.099

Table 4. Coefficients for the Extended Antoine Equation Used in This Work

	Genosorb 1753	CH_4	C_2H_6
C_1	88.35	69.14	28.18
C_2	−643.45	−33084	−2666
C_3	−230.59	506.25	8.51
C_4	0.00	0.00	0.00
C_5	−14.76	−3.44	−2.63
C_6	0.00	0.00	0.00
C_7	6.00	2.00	6.00
T/K	(298.15 to 333.15)	(298.15 to 333.15)	(298.15 to 333.42)
P_i^{sat}(kPa) = $\exp(C_1 + [C_2/(T + C_3)] + C_4T + C_5 \ln T + C_6T^{C_7}) \cdot 101.325$			

Table 5. PR-EOS Interaction Parameters for the Gas (1) + Genosorb 1753 (2) System

T/K	δ_{12}	AAD %
	CO_2[21]	
298.15	−0.234 ± 0.007	1.5
313.15	−0.226 ± 0.003	0.8
333.15	−0.237 ± 0.003	0.9
	CH_4	
298.15	−0.391 ± 0.010	13.1
313.15	−0.405 ± 0.010	9.3
333.15	−0.425 ± 0.013	10.9
	C_2H_6	
298.15	−0.244 ± 0.015	7.2
313.15	−0.233 ± 0.017	6.8
333.15	−0.227 ± 0.006	5.5

Activity Coefficient Models (γ_{gas}). Experimentally obtained solubility data can be expressed by the following expression

$$y_i\phi_i^\nu P = x_i\gamma_i f_i^{*L} \tag{2}$$

where P is the total pressure; y_i is the vapor mole fraction; and x_i is the liquid mole fraction. The vapor phase fugacity coefficients ($\varphi_i^{\ \nu}$) were calculated from the Redlich−Kwong−Soave equation of state (SRK-EOS) with the Wong−Sandler[35] mixing rules. The molar volume, ν_i, was calculated from the modified Rackett equation of Spencer and Danner.[36] The liquid phase fugacity coefficients (f_i^{*L}) were calculated using the extended Antoine equation and SRK-EOS as follows

$$f_i^{*L} = \frac{\phi_i^\nu(T, P_i^{sat})P_i^{sat} \exp\left(\frac{1}{RT}\int_{P_i^{sat}}^p v_i^L dp\right)}{P} \tag{3}$$

where P_i^{sat} is the vapor pressure of the pure component at the system temperature T, and ϕ_i^ν is the vapor fugacity coefficient of the pure component at T and P_i^{sat}. ν_i^l is the liquid molar volume at T and P. The maximum likelihood principle was used to minimize the objective function (Q) to predict the

interaction parameters in activity coefficient models

$$Q = \sum_{n=1}^{NDG} w_n \sum_{i=1}^{NP} \left[\left(\frac{T_{e,i} - T_{m,i}}{\sigma_{T,i}}\right)^2 + \left(\frac{P_{e,i} - P_{m,i}}{\sigma_{P,i}}\right)^2 + \sum_{j=1}^{NC-1} \left(\frac{x_{e,i,j} - x_{m,i,j}}{\sigma_{x,i,j}}\right)^2 + \sum_{j=1}^{NC-1} \left(\frac{y_{e,i,j} - y_{m,i,j}}{\sigma_{y,i,j}}\right)^2\right] \tag{4}$$

where NDG is the number of data groups in the regression case; w_n is the weight of data group n; NP is the number of points in data group n; NC is the number of components present in the data group; T, P, x, and y are temperature, pressure, liquid, and vapor mole fractions; e is the estimated data; m is the measured data; i is the data for data point i; j is the fraction data for component j; and σ is the standard deviation of the individual data.

Three activity coefficient models [Wilson equation,[22] Van Laar model,[23] NRTL model[24]] were used to correlate the solubility data. AAD % values were calculated from the predicted pressures: [at 298.15 K, AAD % values for CH_4: Wilson −4.5; Van Laar −4.6; NRTL − 4.4; AAD % values for C_2H_6: Wilson −4.0; Van Laar −4.2; NRTL − 3.6]. The NRTL model fitted the data very well. Randomness factors (α) for the NRTL model were regressed from 0 to 0.3 to correlate the data. The obtained parameters for all temperatures (298.15, 313.15, and 343.15) K are listed in Table 6 with their % AADs. For CH_4, the α value reduced to 0, indicating that the Genosrob 1753 and CH_4 system is more random. It is known

Table 6. Binary Parameters of the NRTL Equation for the Gas (1) + Genosorb 1753 (2) System

T/K	τ_{12}	τ_{21}	α	% AAD
		CO_2[21]		
298.15	−2.208	4.653	0.3	1.9
313.15	−2.197	4.385	0.3	1.1
333.15	−2.25	4.119	0.3	1.2
		CH_4		
298.15	71.68	−75.33	0	4.4
313.15	71.15	−75.25	0	5.6
333.15	70.51	−75.13	0	2.7
		C_2H_6		
298.15	1961.69	−1.56	0.1	3.6
313.15	1963.53	−1.73	0.1	2.7
333.15	1965.72	−1.93	0.1	1.0

that CH_4 is a symmetrical molecule and the electronegativities of the carbon and hydrogen are almost the same, very much a nonpolar molecule compared to C_2H_6 and CO_2. Renon et al.[24] suggested that the value of α is a function of the coordination number of the molecule (Z) which depends on the polarity and electronegativity of the molecule ($\alpha = 1/Z$). The predicted solubility curves are shown in Figures 2 and 3 along with their experimental solubility data for CH_4 and C_2H_6 in Genosorb 1753.
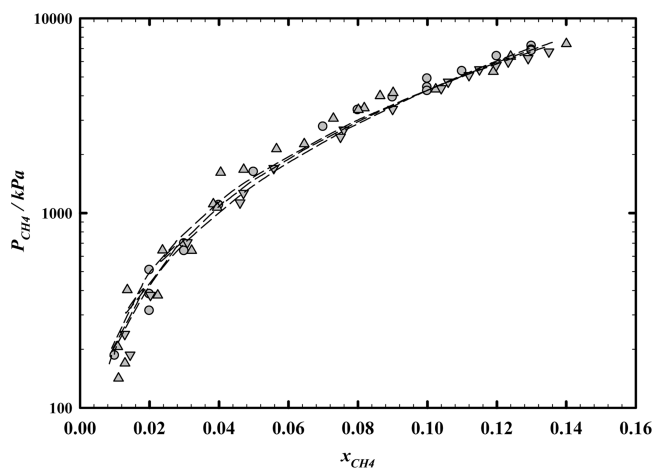
Figure 2. Solubility of methane (CH_4) in Genosorb1753: O, 298.15 K; Δ, 313.15 K; ∇, 333.15 K; ----, NRTL model.
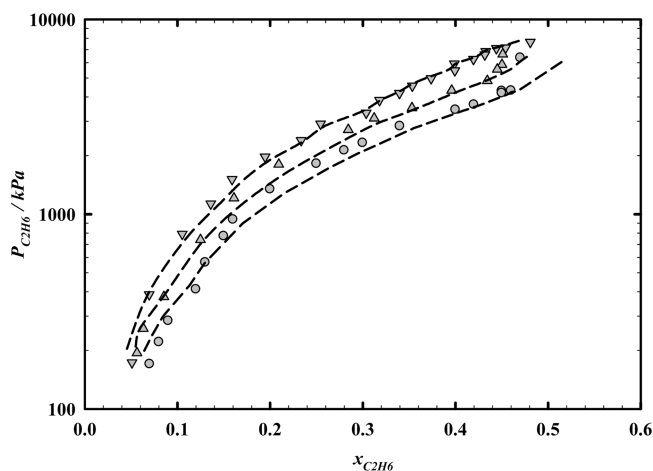

Figure 3. Solubility of ethane (C_2H_6) in Genosorb1753: O, 298.15 K; Δ, 313.15 K; ∇, 333.15 K; ----, NRTL model.

The NRTL equation used in the model is given as

$$\ln \gamma_1 = x_2^2 \left\{ \tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right\} \quad (5)$$

$$G_{12} = \exp(-\alpha \tau_{12}) \quad (6)$$

$$G_{21} = \exp(-\alpha \tau_{21}) \quad (7)$$

The calculated activity coefficients for CO_2, CH_4, and C_2H_6 at each temperature (298.15, 313.15, and 333.15) K are given in Tables 1 and 2. The uncertainty in the calculation depends on the prediction of pressure and mole fraction, which were estimated to be 5 %. The calculated activity coefficients of C_2H_6 and CH_4 were estimated to be less accurate than those of CO_2. Using the predicted activity coefficients, the data for the three systems are reported to be thermodynamically consistent.

Comparison of the Solubility of CO_2 in Different Physical Solvents. High-pressure solubilities of CO_2 in Genosorb 1753 were compared with other promising solvents proposed for natural gas sweetening reported by Henni and Mather.[10] The solubility of CO_2 in physical solvents used in gas processing ranked as:

Diethylene glycol (DEG)[37] < Triethylene glycol (TEG)[38] < Methanol[39] < Ethanol[40] < 1-Propanol[41] < 1-Butanol[40] < 1-Pentanol[42] <1-Octanol[43] < 1,2,3,4-Tetrahydronapthalene[44] < Sulfolane[45] < *N,N*-dimethyl formamide[46]< *N*-formyl morpholine (NFM)[47] < Propylene carbonate[48] < TEGMME[26] < Dimethyl ether (DME)[49] < Diethyl polyethylene glycol (DEPEG)[9] < **Genosorb 1753**.

Figure 4 shows the comparison of the solubility of CO_2 in different physical solvents at 313.15 K. It was observed that
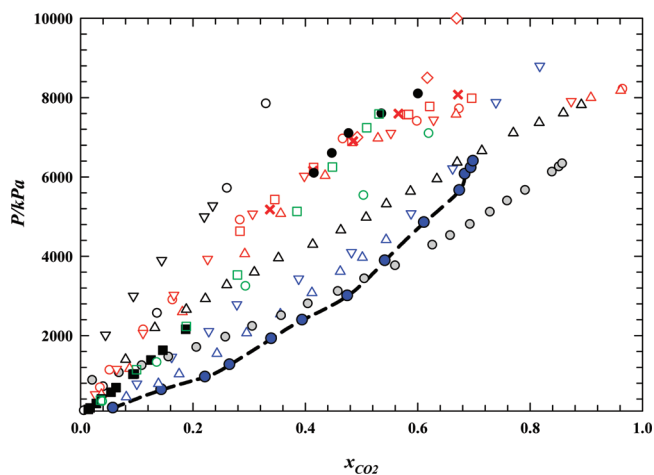

Figure 4. Solubility of CO_2 in several promising physical solvents at 313.15 K: black open down triangle, DEG;[37] black open circle, TEG;[38] red open circle, Methanol;[39] red open down triangle, Ethanol;[40] red open up triangle, 1-Propanol;[41] red open box, 1-Butanol;[40] red ×, 1- Pentanol;[42] red open diamond, 1-Octanol;[43] black filled circle, 1,2,3,4-tetrahydronapthalene;[44] green open box, Sulfolane;[45] black open up triangle, *N,N*-Dimethylformamide;[46] green open circle, NFM;[47] black filled box, Propylene carbonate;[48] blue open down triangle, TEGMME;[26] gray filled circle, DME;[49] blue open up triangle, DEPEG;[9] dashed line with blue filled circle, Genosorb 1753 (this work).

Genosorb 1753 absorbs more CO_2 than all other physical solvents (any other solvent reported in ref 10 had a much lower boiling point to the extent that they could not be used economically in gas sweetening due to high losses in the absorber and regenerator). Diethyl polyethylene glycols and dimethyl ethers have higher capacity for CO_2 absorption. An increase in the partial pressure of CO_2 increased the solubility of CO_2 in Genosorb 1753 and remained the same near $x_{CO_2} = 0.7$.

Comparison of the Solubility of CH_4 in Different Physical Solvents. High-pressure solubilities of CH_4 in Genosorb 1753 were compared with other promising solvents proposed for natural gas sweetening as reported by Henni and Mather.[10] The solubility of CH_4 in physical solvents was as follows:

Water[50] < TEGMME[51] < Sulfolane[45] < TEG[38] < NFM[47] < Methanol[52] < Ethanol[53] < 1-Propanol[53] < **Genosorb 1753** < DME[54] < Diethyl ether (DEE).[54]

Figure 5 shows the comparison of the solubility of CH_4 in different physical solvents at 313.15 K. It was observed that ethers absorb more methane than glycols. Unfortunately, Genosorb 1753 absorbs more CH_4 than other physical solvents like alcohols and glycols but less than diethyl ether and dimethyl ethers. An increase in the partial pressure of CH_4 increased the solubility of CH_4 in Genosorb 1753. Solvents having higher
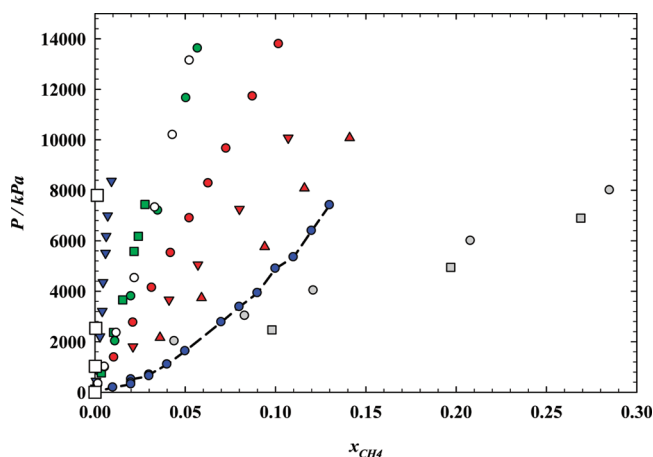
Figure 5. Solubility of CH_4 in several promising physical solvents at 313.15 K: black open box, water;[50] blue filled down triangle, TEGMME;[51] green filled box, Sulfolane;[45] black open circle, TEG;[38] green filled circle, NFM;[47] red filled circle, Methanol;[52] red filled down triangle, Ethanol;[53] red filled up triangle, 1- Propanol;[53] dashed line with blue filled circle, Genosorb 1753 (this work); gray filled circle, DME;[53] gray filled box, DEE.[53]

capacity for methane absorption are of interest to researchers working in the field of energy storage.[10] Henni and Mather et al.[10] suggested TEGMME as a good solvent for processing natural gas because of its low absorption capacity for CH_4.

Comparison of the Solubility of C_2H_6 in Different Physical Solvents. The high-pressure solubility of C_2H_6 in Genosorb 1753 was also compared to that in other promising solvents. The solubility of C_2H_6 in physical solvents was as follows:

Water[55] < Sulfolane[45] < TEG[38] < NMP[56] < TEGMME[57] < Ethanol[53] < 1-Propanol[53] < **Genosorb 1753** < Dimethyl ether polyethylene glycols (DMEPEG).[58]

Figure 6 shows the comparison of the solubility of C_2H_6 in different physical solvents at 313.15 K. It can be observed that
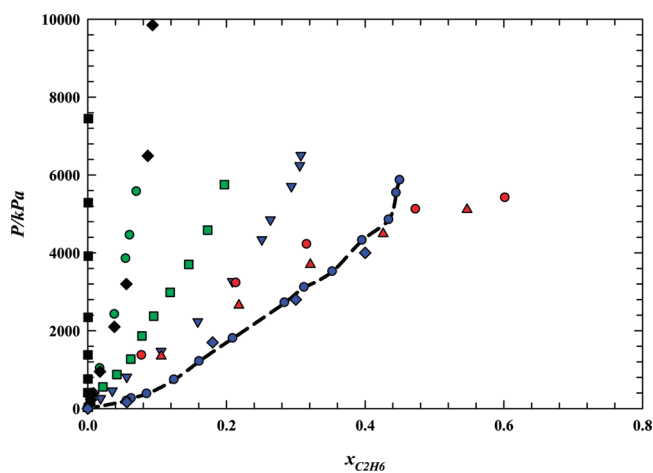

Figure 6. Solubility of C_2H_6 in several promising physical solvents at 313.15 K: black filled box, Water;[55] green filled box, Sulfolane;[45] black filled diamond, TEG;[38] green filled circle, NMP;[56] blue filled down triangle, TEGMME;[57] red filled circle, Ethanol;[53] red up triangle, 1-Propanol;[53] blue filled diamond, DMPEG;[58] dashed line with blue filled circle, Genosorb 1753 (this work).

alcohols absorb more ethane than glycols and ethers. Genosorb 1753 absorbs more ethane than some solvents presently used in

the gas sweetening industry (Sulfolane, NFM, and NMP). This study also confirms that the best physical solvents for absorbing acid gases have the disadvantage of absorbing large amounts of ethane.[59]

Derived Thermodynamic Properties for CO_2, CH_4, and C_2H_6 in Genosorb 1753. *Excess properties (G^E, H^E, and S^E).* Because of the good fit for the solubility data with the NRTL equation, it will be interesting to study the behavior of the solution properties from the derived excess properties. Using the NRTL parameters, excess properties such as excess enthalpies (H^E), entropies (S^E), and Gibb's free energies (G^E) can be derived.

The excess enthalpy is derived by the Gibbs–Helmholtz relation as follows

$$\frac{H^E}{RT} = -\left[\frac{T\partial\left(\frac{G^E}{RT}\right)}{\partial T} \right]_{P,x} \quad (8)$$

The excess Gibbs energy, excess enthalpy, and excess entropy are all related by

$$H^E = G^E + TS^E \quad (9)$$

The excess Gibbs energy form of the NRTL equation (Gennero de Chialvo[60]) is

$$G^E = -\frac{RT}{\alpha} x_1 x_2 \left[\frac{G_{21} \ln G_{21}}{(x_1 + G_{21}x_2)} + \frac{G_{12} \ln G_{12}}{(x_2 + G_{12}x_1)} \right] \quad (10)$$

The excess entropy form of the NRTL equation (Gennero de Chialvo[60]) is

$$S^E = -\frac{R}{\alpha} x_1 x_2 \left[\frac{x_1 G_{21}(\ln G_{21})^2}{(x_1 + G_{21}x_2)^2} + \frac{x_2 G_{12}(\ln G_{21})^2}{(x_2 + G_{12}x_1)^2} \right] \quad (11)$$

and

$$G_{ij} = \exp\left[\frac{-\alpha(\Delta g_{ij})}{RT} \right] \quad (12)$$

where, $i = 1,2$ and $j = 1,2$.

The fitted parameters for the solubility data of the gases were used to calculate G^E, TS^E, and H^E at each temperature. The calculated excess properties for (Genosorb 1753–CO_2) and (Genosorb 1753–C_2H_6) systems are presented in Figures 7, 8, and 9. For CH_4, the excess properties could not be predicted because of the negligible randomness factor ($\alpha = 0$). The minimum excess enthalpy for the mixing in Genosorb 1753 occurred for CO_2 at $x_{CO_2} = 0.4$ and at $x_{C_2H_6} = 0.6$ for C_2H_6. All calculated excess properties of Genosorb 1753 from the gases and their changes with respect to mole fractions indicated that the excess properties for C_2H_6 are higher than those for CO_2 because of its nonideal behavior.

The temperature-dependent form of the NRTL energy parameters Δg_{12} and Δg_{21} were calculated from the fitted
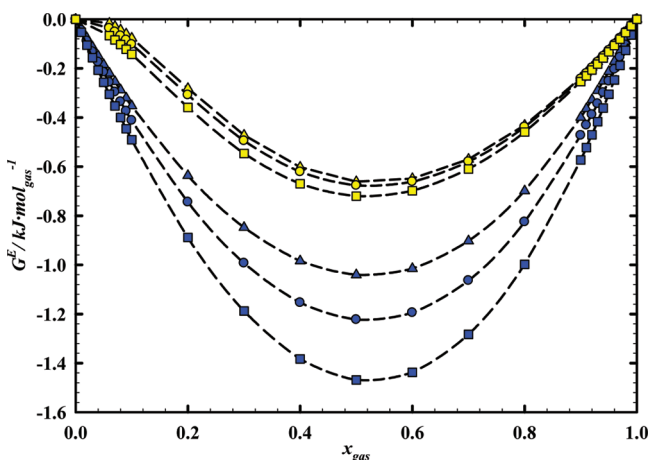
Figure 7. Excess Gibbs free energy for the solubility of CO_2 and C_2H_4 in Genosorb 1753 at different temperatures: blue filled up triangle, C_2H_6 at 298.15 K; blue filled circle, C_2H_6 at 313.15 K; blue filled box, C_2H_6 at 333.15 K; yellow filled up triangle, CO_2 at 298.15 K; yellow filled circle, CO_2 at 313.15; yellow filled box, CO_2 at 333.15 K.
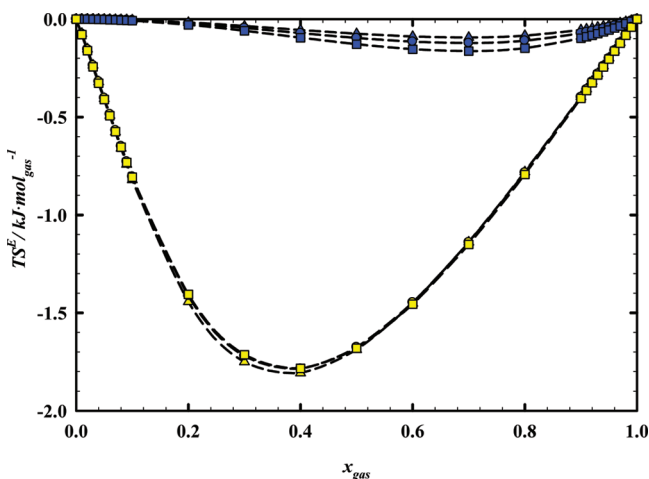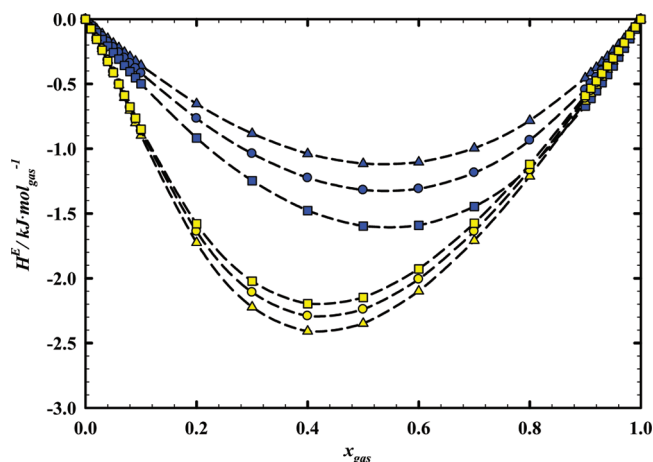

Figure 8. Excess entropy for the solubility of CO_2 and C_2H_4 in Genosorb 1753 at different temperatures: blue filled up triangle, C_2H_6 at 298.15 K; blue filled circle, C_2H_6 at 313.15 K; blue filled box, C_2H_6 at 333.15 K; yellow filled up triangle, CO_2 at 298.15 K; yellow filled circle, CO_2 at 313.15; yellow filled box, CO_2 at 333.15 K.

parameters τ_{12} and τ_{21} at each temperature as shown in equation:=

$$\tau_{12} = \left[\frac{\Delta g_{12}}{RT}\right] \qquad \tau_{21} = \left[\frac{\Delta g_{21}}{RT}\right] \tag{13}$$

Δg_{12} and Δg_{21} are linearly dependent with temperature. Therefore, a linear temperature dependence model as suggested by Hanks et al.[61] and Demirel[62] for Δg_{12} and Δg_{21} was used to calculate the excess properties. The linear form used was

$$\Delta g_{12} = a + b(T - 298.15) \tag{14}$$

$$\Delta g_{21} = c + d(T - 298.15) \tag{15}$$

The regressed parameters for the equations are

For CO_2: $a = -5467.01$ $b = 0.77$ $c = 11498.09$

$d = -37.62$

Figure 9. Excess enthalpy for the solubility of CO_2 and C_2H_4 in Genosorb 1753 at different temperatures: blue filled up triangle, C_2H_6 at 298.15 K; blue filled circle, C_2H_6 at 313.15 K; blue filled box, C_2H_6 at 333.15 K; yellow filled up triangle, CO_2 at 298.15 K; yellow filled circle, CO_2 at 313.15; yellow filled box, CO_2 at 333.15 K.

For CH_4: $a = 177696.72$ $b = 502.81$

$c = -186734.89$ $d = -610.84$

For C_2H_6: $a = 4862681.45$ $b = 16628$

$c = -3862.93$ $d = -42.72$

Equations 14 and 15 can be used with the NRTL equation to interpolate the excess properties and activity coefficients between (298.15 and 333.15) K. Extrapolations can be made with caution and are suggested to be within (288.15 to 343.15) K.[15]

Henry's Law Constants. Since the NRTL model represented data the best, Henry's Law constants were calculated from the NRTL parameters using the Henry's Law relation proposed by Prausnitz et al.[63]

$$H_{12} = \gamma_{1,2}^{\infty} f_1^{\circ L} \tag{16}$$

where

$$\gamma_{1,2}^{\infty} = \tau_{21} + \tau_{12} \exp(-\alpha_{12}\tau_{12}) \tag{17}$$

Table 7 shows the comparison of Henry's law constants calculated for CO_2, CH_4, and C_2H_6. The Henry's law constant

Table 7. Calculated Infinite Dilution Activity Coefficients and Henry's Law Constants Based on the NRTL Equation for Different Gases in Genosorb 1753

	CO_2		CH_4		C_2H_6	
T/K	$\gamma_{CO_2}^{\infty}$	H_{CO_2}	$\gamma_{CH_4}^{\infty}$	H_{CH_4}	$\gamma_{C_2H_6}^{\infty}$	$H_{C_2H_6}$
298.15	0.14	3.75	0.026	48.05	0.210	6.40
313.15	0.11	4.90	0.017	43.48	0.177	8.35
333.15	0.09	6.81	0.010	40.13	0.145	12.41

and the infinite dilution activity coefficient dependence are similar to those for pure glymes.[6] The solubility of CO_2 and C_2H_6 decreased with an increase in temperature, whereas the solubility of CH_4 increased with temperature. Similar solubility behavior was observed in TEGMME by Henni et al.[51]

Differential Enthalpy of Solution at Infinite Dilution. The enthalpy of solution (i.e., gaseous solute−solvent interaction) is the heat produced when 1 mol of solute is mixed with a solvent to form a solution. In the dilute region, the enthalpy of solution is the sum of the partial molar enthalpy of mixing (i.e., a measure of the liquid solute−solvent interaction) and the enthalpy of condensation[64], and it is determined by the variation of Henry's Law constant with temperature. Sciamanna[6] derived the differential enthalpy of solution for nonvolatile solvents and a dissolved solute at low pressures as

$$\overline{\Delta H}_{gas}^{Soln} = R \left[\frac{\partial \ln H_{12}}{\partial \left(\frac{1}{T} \right)} \right]_{P, x_{gas}} \tag{18}$$

where $\overline{\Delta H}_{gas}^{Soln}$ is the enthalpy of solution at infinite dilution ($kJ \cdot mol_{gas}^{-1}$) and R is the universal constant (0.008314 $kJ \cdot mol^{-1} \cdot K^{-1}$). The values of $\overline{\Delta H}_{gas}^{Soln}$ were found to be -14.65 $kJ \cdot mol_{CO_2}^{-1}$, 4.48 $kJ \cdot mol_{CH_4}^{-1}$, and -10.15 $kJ \cdot mol_{C_2H_6}^{-1}$. The differential enthalpies of solution for CO_2 and C_2H_6 in Genosorb 1753 were negative, indicating an exothermic process. For CH_4, it was positive, indicating an endothermic absorption process.

Partial Molar Enthalpy of Mixing. The enthalpy change due to solute and solvent interactions in the liquid phase is defined as the partial molar enthalpy of mixing,[64] and more specifically it can be defined as the enthalpy change when pure species are mixed to form 1 mol of solution. The greater the enthalpy of mixing, the greater the interaction between the solute and solvent, and the smaller the activity coefficient of the solute in the solution. The partial molar enthalpy of mixing is negative for a strong solute−solvent interaction which indicates exothermic reaction of the system. It is defined as

$$\overline{\Delta H}_{gas}^{Mix} = R \left[\frac{\partial \ln \gamma_{gas}^{\infty}}{\partial \left(\frac{1}{T} \right)} \right]_{P, x_{gas}} \tag{19}$$

where $\overline{\Delta H}_{gas}^{Mix}$ is the partial molar enthalpy of mixing at infinite dilution ($kJ \cdot mol_{gas}^{-1}$) and R is the universal constant 0.008314 $kJ \cdot mol^{-1} \cdot K^{-1}$. The value of $\overline{\Delta H}_{gas}^{Mix}$ was found to be -11.17 $kJ \cdot mol_{CO_2}^{-1}$; 8.87 $kJ \cdot mol_{C_2H_6}^{-1}$ for C_2H_6, and 23.17 $kJ \cdot mol_{CH_4}^{-1}$ for the case of CH_4. These results indicate that these light hydrocarbons exhibit low solute−solvent interaction depending upon their polarities.

Differential Enthalpy of Solution. Using the NRTL equation as a predictive model, the differential enthalpy of solution (absorption) for the gas into Genosorb 1753 was determined based on the following Clausius−Clapeyron equation

$$\Delta H_{gas}^{Abs} = R \left[\frac{d \ln P_{gas}}{d \left(\frac{1}{T} \right)} \right]_{P, x_{gas}} \tag{20}$$

where ΔH_{gas}^{Abs} is the enthalpy of absorption ($kJ \cdot mol_{gas}^{-1}$), and R is the universal constant (0.008314 $kJ \cdot mol^{-1} \cdot K^{-1}$). The

calculated values of the enthalpy of absorption for gases (CO_2, CH_4, and C_2H_6) are plotted in Figure 10. The enthalpy
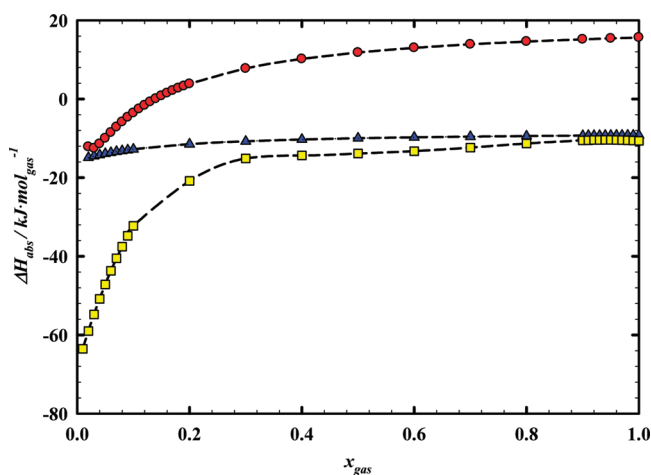
Figure 10. Calculated enthalpy of absorption (solution) for CO_2, CH_4, and C_2H_4 in Genosorb 1753 in the temperature range of (298.15 to 333.15) K: yellow filled box, CO_2; blue filled triangle, C_2H_6; red filled circle, CH_4.

of absorption showed a nonlinear dependence in the low mole fraction region and became linear at higher concentration for CO_2 and C_2H_6. For CO_2, the enthalpy of absorption approaches linear dependence in the region of $x_{CO_2} = 0.3$ to 1, and for C_2H_6 the linear dependence was around $x_{C_2H_6} = 0.4$ to 1, indicating that the liquid is saturated with the gas. The enthalpy of absorption decreased with the increase in the mole fraction of CH_4. The positive values of the enthalpy of absorption became negative after $x_{CH_4} = 0.13$, indicating that the liquid phase became saturated with CH_4 and needs more heat to absorb more CH_4 in the system (i.e., endothermic process).

Selectivity of Genosorb 1753 for CO_2, CH_4, and C_2H_6. Different promising physical solvents were ranked by Henni et al.[12] to choose the best solvent for CO_2 removal from natural gas while absorbing the least amount of CH_4 and C_2H_6. The following function was used for the ranking

$$Selectivity/MPa^{-1} = \frac{H_{CO_2}}{H_{CH_4} \cdot H_{C_2H_6}} \tag{21}$$

The ranking in terms of selectivity (lowest is the best) was found to be:
Sulfolane[12] < TEGMME[11] < NFM[12] < NMP[12] < PEGDME 250[12] < **Genosorb 1753** < TTEGDME[12] < TEGMBE[12] < DEGDME[12] < TEGDME.[12]

The ranking is graphically represented in Figure 11 as a function of temperature. The viscosity of these solvents is also an important factor to be considered in screening a good solvent. The viscosities (mPa·s) of best solvents are:
Sulfolane (10.29)[65] > NFM (7.87)[66] > **Genosorb 1753** (7.28)[20] > Selexol (5.8)[67] > TTEGDME (3.38)[68] > TEGDME (1.95)[69] > NMP (1.66).[70]

Though the selectivity of sulfolane is the best among the studied solvents, it has the highest viscosity. NFM is solid at ambient temperature, and it is thought that to be used in commercial process it must be mixed with *N*-acetyl morpholine (NAM) to reduce its freezing point.[12] All the solvents mentioned
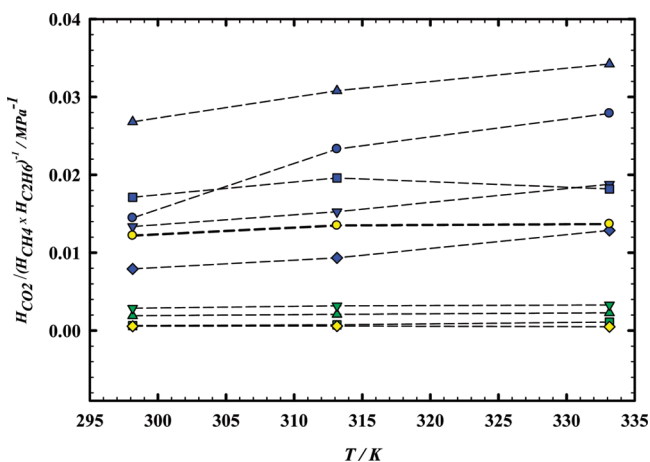
Figure 11. Comparison of the selectivity (capacity for CO_2 absorption and coabsorption of CH_4 and C_2H_6) as a function of temperature (T) for different physical solvents: blue filled up triangle, TEGDME;[12] blue filled circle, DEGDME;[12] blue filled square, TEGMBE;[12] dashed line with filled yellow circle, Genosorb 1753 (this work); blue filled down triangle, TTEGDME;[12] blue filled diamond, PEGDME 250;[12] green filled up triangle, NFM;[12] green filled down triangle, NMP;[12] green filled box, Sulfolane;[12] yellow filled diamond, TEGMME.[11]

above (Sulfolane, NFM, NMP, and Selexol) have found wide commercial application in gas sweetening operations.

Most of the industrial natural gas streams are rich in CH_4 and CO_2 with traces of C_2H_6. If the gas stream has negligible amounts of C_2H_6, then the ranking of solvents in terms of selectivity (CO_2 vs CH_4) will be: TEGMME < Sulfolane < NFM < NMP < **Genosorb 1753** < TTEGDME < PEGDME 250 < TEGMBE < TEGDME < DEGDME. The composition of mixtures like Selexol and Genosorb 1753 may be tailored/optimized to the composition of the gas stream in the field.

CONCLUSION

In this study, the solubilities of CH_4 and C_2H_6 in mixed polyglycol dimethyl ethers (Genosorb 1753) were measured at (298.15, 313.15, 323.15, and 333.15) K. The Peng−Robinson equation of state was found to correlate the data with an objective function of 12 % for CH_4 and 6.5 % for C_2H_6. A comparison study on the solubilities of CO_2, CH_4, and C_2H_6 in Genosorb 1753 with other physical solvents revealed that the capacity for CO_2 absorption is greater for Genosorb 1753 than other physical solvents, but the coabsorption of C_2H_6 was also large. The NRTL activity coefficient model was used to correlate the data within 4 % for CH_4 and 3 % for C_2H_6. Using the calculated NRTL parameters, the excess enthalpies were calculated for the full composition range of CO_2, CH_4, and C_2H_6 in the liquid phase, and the results suggest strong interactions between CO_2 and Genosorb 1753, with weaker interactions with CH_4 and C_2H_6. The heat effects accompanying the absorption were also calculated. The selectivity of Genosorb 1753 for natural gas sweetening was calculated (0.0122, 0.0135, and 0.0137 MPa^{-1} at 298.15, 313.15, and 343.15 K) and compared to other physical solvents like Sulfolane and NMP along with their viscosity data. The study confirms the high CO_2 absorption capacity of Genosorb 1753 and a low coabsorption of CH_4 but also what seems to be a high coabsorption of ethane. Genosorb 1753 and Selexol as mixtures of ether glycols can be tailored (optimum composition) to improve their selectivity. Finally, the study also shows why solvents like Sulfolane, NMP, NFM, and

Selexol have found commercial application in many gas sweetening operations.

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