

Chemical Capture of CO₂ by Glycine Salt Solution

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The role of carbon dioxide in global warming is one of the contemporary environmental issues, making necessary access to the technologies capturing the released CO₂ into the atmosphere. Amino acids have the same amine functionalities as alkanolamines with similar behavior towards CO₂ absorption. The solubility of carbon dioxide in potassium glycinate (KG) solutions with different concentrations at various temperatures was measured. On the basis of the results, the mole of CO₂ adsorbed, $n_{CO_2, adsorbed}$, increases by temperature and the concentration of KG. The $n_{CO_2, adsorbed}$ versus the KG concentration at different temperatures was fitted with a sigmoidal function, so that the moles of CO₂ adsorbed can be reproduced in the temperature range of 300.15-327.15 K and the concentrations of 0.01-1.00 M of KG within the experimental errors.

Keywords: CO₂ removal, Solubility parameter, Potassium Glycinate

INTRODUCTION

The role of carbon dioxide in global warming is one of the most important contemporary environmental issues making necessary access to the technologies minimizing the discharge of CO₂ into the atmosphere. Among the global warming disasters, melting icebergs and expansion of oceans have a strong impact on the environment. This will cause droughts, deforestation, disruption of ecosystems, extensive bleaching of coral reefs, increasing forest fire activity, floods and extreme temperature on crop production, and production of heat waves [1,2]. Sea levels have risen about 10-20 cm during the past century. Intergovernmental Panel on Climate Change predicted that by year 2100 the rise in sea levels would be between 20 cm and 88 cm [1].

The generation of CO₂ is inevitable due to the combustion of fossil fuels. The efficient capture of CO₂ from industrial operations is considered as a vital strategy to reduce atmospheric CO₂ level significantly. There are three

main approaches to capture CO₂ [3]:

- (1) Post-combustion: involving the removal of CO₂ from the flue gas produced by combustion.
- (2) Oxy-fuel combustion: burning fossil fuels such as coal, oil, or natural gas using pure oxygen instead of air as the primary oxidant.
- (3) Pre-combustion: capturing CO₂ from fossil fuels before the fuel is burned [4].

There are numerous post-combustion gas separation technologies, namely adsorption, membrane separation, cryogenic separation, micro-algal bio-fixation, and absorption [3]. In absorption, molecules, atoms, or ions in a gas or liquid phase diffuse to the surface of a solid and bond with the solid surface. Several absorbents have been proposed for CO₂ capturing including carbon fiber monolithic adsorbents [5], activated carbon fiber, phenolic resin composites, melamine-formaldehyde highly porous adsorbent, and amine immobilized adsorbents [3].

Cryogenic process also known as low temperature distillation is an alternative approach to conventional flue gas emission remediation. The flue gas containing high concentration of carbon dioxide (>50%) is cooled and

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liquefied. The application of cryogenic processes to the flue gas emission remediation is still at an early stage of application [6].

CO₂ can also be fixed from several sources such as the atmosphere and industrial exhaust gases by microalgae, photosynthetic microorganisms [7]. Furthermore, CO₂ from the flue gases may be recovered by absorption [8]. There are three basic types of chemical, physical, and hybrid absorptions. In chemical absorption, CO₂ reacts with one or more basic chemical absorbent and a weakly bonded intermediate compound is formed. Then, this compound is broken down by heat, regenerating the original absorbent and producing a CO₂ stream. Typical commercial absorbents are aqueous solutions of amines such as monoethanolamine, diethanolamine, or N-methyldiethanolamine (MDEA) [9]. The disadvantages of these absorbents are high volatility, chemical instability in the presence of O₂, and corrosivity [10]. In physical absorption, CO₂ is physically absorbed in a solvent according to Henry's law and then regenerated using either heat or pressure reduction or both [11]. According to Henry's law, the concentration of a solute gas, *C*, in a solution is directly proportional to the partial pressure of gas, *P*, above the solution:

$$P = K_H C \quad (1)$$

where *K_C* is Henry's constant. Selexol (dimethylether of polyethylene glycol) and Rectisol (cold methanol) are typical absorbents applied at high pressure [12]. At lower pressures, the chemical absorption processes are more economical. Chemical absorption has advantages over physical absorption, including lower capital and operational cost, stripping process which follows the absorption, and lower energy consumption [12].

In hybrid absorption, a combination of the best characteristics of both chemical and physical absorbents are used. Typical absorbent used in this type of absorption is Sulfinol (a composite solvent, consisting of a mixture of MDEA, sulfolane (tetrahydrothiophene dioxide), and water) [12].

When choosing a solvent for the chemical absorption process, CO₂ absorption rate, CO₂ solubility, heat of absorption, solvent volatility, and stability as well as its environmental safety and price should be considered [13].

Available solvents are almost exclusively based on aqueous solutions of alkanolamines; molecules carrying both hydroxyl and amine functional groups on an alkane backbone. CO₂ absorption into alkanolamine solutions occurs mainly as a result of the amine group of the alkanolamine molecule. It has been suggested that at a very high pH, CO₂ can react with the hydroxyl groups of the molecule. However, this reaction is generally not expected to play a significant role in industrial CO₂ capture processes, as the pH of the systems is usually not high enough. Different types of amines vary significantly in how they react with CO₂, in respect to both mechanism and kinetics [14].

Amino acids have the same amine functionality as alkanolamines. Alkaline amino acid salt solutions behave similar towards CO₂ absorption. Compared to the solutions of alkanolamines, amino acid salt solutions are characterized by low vapor pressures, higher stability towards oxidative degradation and expected to be environmentally friendly as amino acids are omnipresent in nature [15].

When absorbing CO₂ into amino acid salt solutions, precipitation of the reaction products may occur. The appearance of solids offers interesting advantages as well as drawbacks. The main negative aspects are the possible plugging and fouling of the gas-liquid contactors and heat-transfer surfaces. The advantages are explained by the fact that the precipitation of the reaction products decreases their concentration in the liquid phase, shifting the reactions towards the formation of more products, thereby, increasing the CO₂ absorption by the solvent [16]. Recently, several works have been published on the use of ionic liquids (ILs) as promising absorbents to absorb CO₂ due to their negligible vapor pressure at room temperature, non-flammability, and structural designability [17-19]. The ILs are salts consist of anions and cations but unlike common salts they are liquids at room temperature [20]. The CO₂ capture can be enhanced by introducing some functional groups to either anion or cation of an IL [21]. Yan *et al.* [22] used a mixed solvent system consisting of amino acid IL (cholinium glycinate) and amine solution (MDEA) as a CO₂ absorbent. They showed that the reactivity of MDEA towards CO₂ absorption is improved by adding the ionic liquid.

The purpose of the present work is to measure the solubility of carbon dioxide in potassium glycinate solution with various concentrations and at different temperatures. Amino acids react with CO₂ via a zwitterion mechanism in an alkaline solution [22]. The kinetically dominant reaction is the direct reaction between CO₂ and the amino acid salt to form a carbamate and the protonated amino acid.

MATERIALS AND METHODS

Materials

Sodium hydroxide (Fluka, 97%), potassium hydroxide (Riedel, 85%), phenolphthalein (Riedel), calcium carbonate (BDH, 98%), and potassium hydrogen phthalate (BDH, 99/9%) were utilized as received with no further purification. Glycine (99%), hydrochloric acid (37%) and methyl orange were purchased from Merck. The distilled water was used for the preparation of all solutions including CO₂ and KG.

Preparation of Potassium Glycinate Solution

Potassium glycinate solutions with different concentrations (0.01-1 M) were prepared through neutralizing equimolar solutions of potassium glycinate and potassium hydroxide.

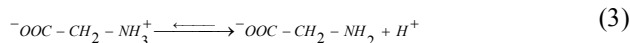
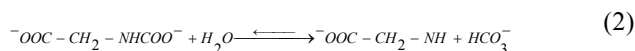
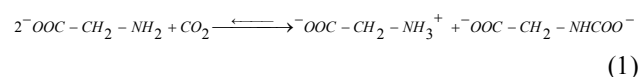
HCl (1 M) was used for standardization of each solution. The glycine forms a zwitterion in water and reacts with potassium hydroxide to form KG.

Preparation of CO₂ gas

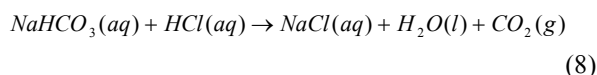
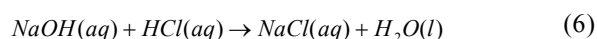
CO₂ gas was prepared from the reaction of excess amount of CaCO₃ with standard HCl. In all experiments, 0.1 mol CO₂ (g) was prepared. For this purpose, in a 500 ml three-neck flask, a certain volume of HCl standard solution (8 M) was added to 0.11 mol of CaCO₃.

Determination of the Amount of CO₂ Absorbed

200 ml of potassium glycinate solution with a specified concentration was transferred to a three-neck flask in a water bath (SSB4, Grant Instruments) with controlled temperature. The following reactions occur:



CO₂ was produced from the reaction of CaCO₃ with standard HCl and introduced as bubbles into KG solution. When no bubble was observed in the solution, N₂ gas was blown as a carrier gas into the solution for 5 min to ensure that all CO₂ produced was entered into KG solution. A certain amount of prepared CO₂ was absorbed by KG and the remaining was added into two-neck flask containing NaOH (0.5 M) and stirred. Then, the solution was transferred to a beaker and titrated by HCl (2 M) standard solution. At this point, pH meter (MARTINI/MI 151) was used to calculate the pH solution. The potentiometric titration curve was plotted. All titration graphs had three equivalence points:



The mole of CO₂ adsorbed, $n_{\text{CO}_2, \text{absorbed}}$, is given by

$$n_{\text{CO}_2, \text{absorbed}}=n_{\text{CO}_2, \text{initial}}-n_{\text{CO}_2, \text{out}}\quad (9)$$

where $n_{\text{CO}_2, \text{initial}}$ and $n_{\text{CO}_2, \text{out}}$ are the amount of initial and final concentrations, respectively.

The gas solubility or absorption loading, α , can be calculated using the following equation [22]:

$$\alpha=\frac{n_{\text{CO}_2, \text{absorbed}}}{n_{\text{Potassiumglycinate}}}\quad (10)$$

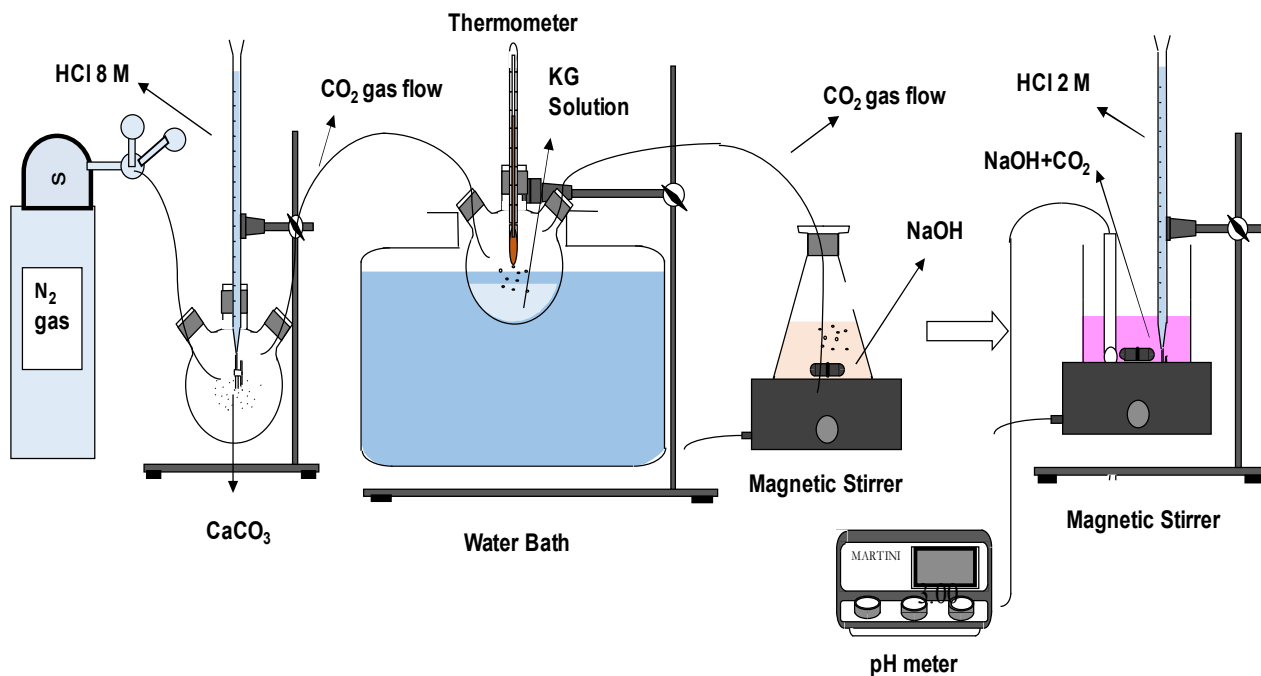


Fig. 1. The schematic diagram of the experimental setup.

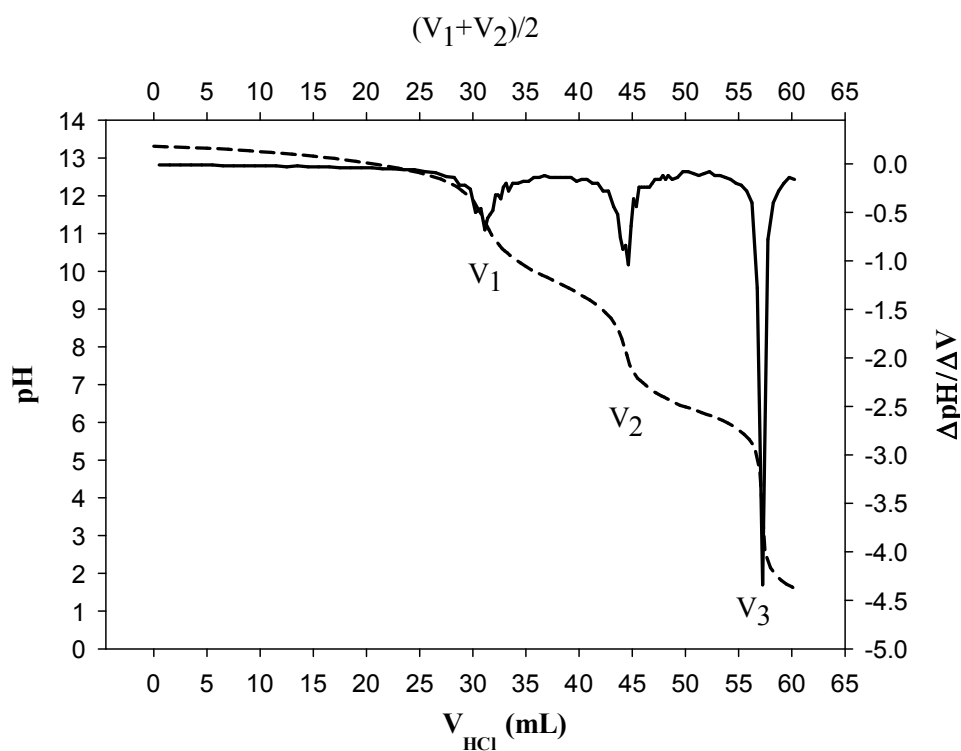


Fig. 2. Typical potentiometric titration curve.

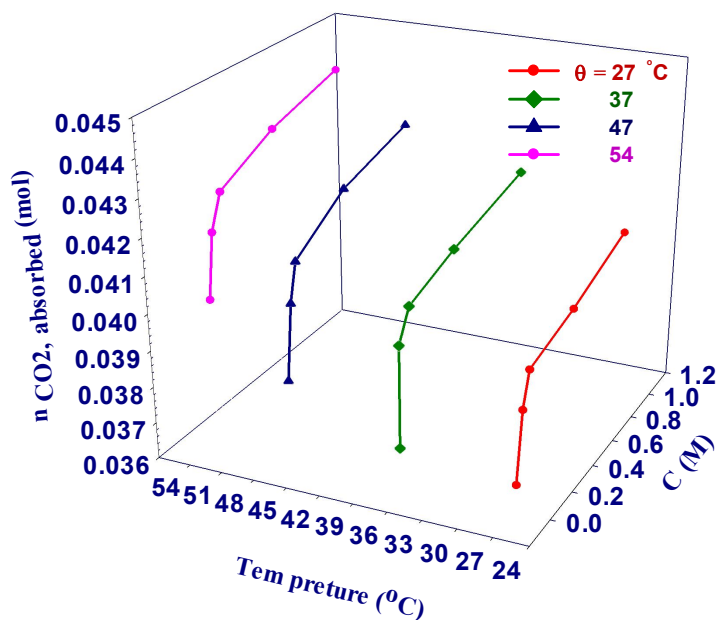


Fig. 3. The 3-D plot between temperature, concentration of KG, and $n_{CO_2,absorbed}$.

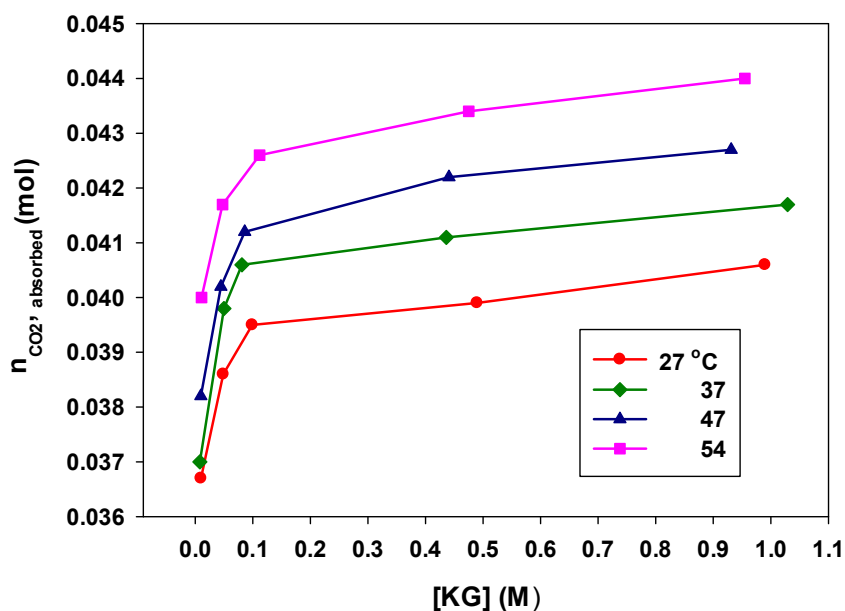


Fig. 4. $n_{CO_2,absorbed}$ against the KG concentration at different temperatures.

Fig. 2 shows a typical pH potentiometric titration curve versus HCl volume added (solid line curve) and $\Delta pH/\Delta V$ versus average volume of HCl (dashed curve) for CO₂

output from 200 ml of 0.08113 M of KG solution at 37 °C. The first, second, and third equivalence points occurred at 38.08, 44.45 and 57.25 ml of HCl, respectively. The

Table 1. $n_{CO_2,absorbed}$ and α at Different Temperatures and Concentrations of KG

θ (°C)	[KG] (M)	$n_{CO_2,absorbed}$ (mol)	$n_{CO_2,absorbed}$ (mol)	α
27	0.0101	0.0221	0.0367	18.0255
	0.0448	0.0202	0.0386	3.9565
	0.0990	0.0193	0.0395	1.9933
	0.4896	0.0189	0.0399	0.4074
	0.9898	0.0182	0.0406	0.2050
37	0.0080	0.0218	0.0370	22.9813
	0.0498	0.0190	0.0398	4.4295
	0.0811	0.0182	0.0406	2.5022
	0.4360	0.0177	0.0411	0.4713
	1.0290	0.0171	0.0417	0.2026
47	0.0098	0.0206	0.0382	19.3202
	0.0446	0.0186	0.0402	4.5047
	0.0859	0.0176	0.0412	2.3986
	0.4407	0.0166	0.0422	0.4787
	0.9310	0.0160	0.0427	0.2297
54	0.0110	0.0188	0.0400	18.0799
	0.0475	0.0171	0.0417	4.3811
	0.1119	0.0162	0.0426	1.9031
	0.4750	0.0154	0.0434	0.4567
	0.9548	0.0148	0.0440	0.2304

Table 2. The Values of a, b, c and R² of Eq. (11)

θ (°C)	a (mol)	b	$c \times 10^{-4}$ (M)	R ²
27	0.0412	-0.5881	2.4650	0.98
37	0.0420	-0.5219	2.0000	0.99
47	0.0441	-0.3337	0.3714	1.00
54	0.0459	-0.2655	0.0812	1.00

Table 3. Constants for Eqs. (12) to (14)

a (mol)			b			c (M)		
a ₀ (mol)	a ₁	R ² (mol °C ⁻¹)	b ₀	b ₁ (°C ⁻¹)	R ²	c ₀ (M)	c ₁ (M °C ⁻¹)	R ²
0.0361	0.0002	0.95	-0.9514	0.0127	0.96	0.0005	-9.7073E-006	0.94

standard concentrations of NaOH (200 ml) and HCl solutions were 0.5482 and 1.8090 M, respectively, in this experiment.

RESULTS AND DISCUSSION

Figure 3 shows the 3-D plot of $n_{CO_2,absorbed}$ as functions of both temperature and concentration of KG. Table 1 gives the values of $n_{CO_2,absorbed}$ and a at different temperatures and concentrations of KG. As this table and figure show, the mole of absorbed CO₂ increases both by temperature and the concentration of KG.

Figure 4 shows $n_{CO_2,absorbed}$ against the KG concentration at different temperatures. Since this curve is S-shape, it was fitted with the following sigmoidal function for each temperature:

$$n_{CO_2,absorbed} = \frac{a}{1 + \left(\frac{[KG]}{c}\right)^b} \quad (11)$$

The values of a , b , c , and the correlation coefficients, R^2 , are given in Table 2. All of these parameters are liner functions of temperature, θ :

$$a = a_0 + a_1\theta \quad (12)$$

$$b = b_0 + b_1\theta \quad (13)$$

$$c = c_0 + c_1\theta \quad (14)$$

where a_0 , a_1 , b_0 , b_1 , c_0 and c_1 are constants and their values

are given in Table 3.

As Tables 2 and 3 show, the values of R^2 for all equations are close to one. A R^2 value close to one does not guarantee a good fitting. Hence, we calculated $n_{CO_2,absorbed}$ for each concentration of KG at different temperatures. The deviation percentage between the experimental and calculated values of $n_{CO_2,absorbed}$ are given in Table 4. The average value percentage of deviations is 2%. Hence, the values of $n_{CO_2,absorbed}$ can be reproduced in the temperature range of 27-54 °C and the concentrations of 0.01-1.00 M of KG within the experimental errors.

CONCLUSIONS

In this work, the solubility of carbon dioxide in glycine salt solution with various concentrations and at different temperatures was measured experimentally. The present work contains the following main conclusions:

1. The absorbed moles of CO₂, $n_{CO_2,absorbed}$ increases both by temperature and the concentration of KG.
2. The absorbed moles of CO₂ versus KG concentrations at different temperatures were fitted with the sigmoidal function, so that the values of $n_{CO_2,absorbed}$ can be reproduced in the temperature range of 27-54 °C and the concentrations of 0.01-1.00 M of KG within the experimental errors.

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Table 4. The Deviation Percentages between the Experimental and Calculated Values of $n_{CO_2,absorbed}$

[KG] (M)	$n_{CO_2,absorbed}$ (mol)		Dev. (%) ^a
	Exp.	Cal.	
$\theta = 27\text{ }^\circ\text{C}$			
0.0101	0.0367	0.0376	-2.4523
0.0448	0.0386	0.0398	-3.1088
0.0990	0.0395	0.0404	-2.2784
0.4896	0.0399	0.0411	-3.0075
0.9898	0.0406	0.0412	-1.4778
37			
0.0080	0.0370	0.0380	-2.7027
0.0498	0.0398	0.0410	-3.0150
0.0811	0.0406	0.0415	-2.2167
0.4360	0.0411	0.0426	-3.6496
1.0290	0.0417	0.0429	-2.8777
47			
0.0098	0.0382	0.0396	-3.6649
0.0446	0.0402	0.0419	-4.2288
0.0859	0.0412	0.0426	-3.3980
0.4407	0.0422	0.0438	-3.7914
0.9310	0.0427	0.0442	-3.5128
54			
0.0110	0.0400	0.0402	-0.5000
0.0475	0.0417	0.0420	-0.7194
0.1119	0.0426	0.0428	-0.4694
0.4750	0.0434	0.0438	-0.9216
0.9548	0.0440	0.0442	-0.4545

$${}^a\%Dev = \frac{(n_{exp} - n_{cal})}{n_{exp}} \times 100$$

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