COMPARISON AMONG PHYSICOCHEMICAL PROPERTIES FOR AMINE SOLVENTS THROUGH GROUP CONTRIBUTION METHODS

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Abstract: The compounds CO_2 and H_2S are acid gases (AG) known to negatively affect the environment due to their corrosion potential. As a solution, amine solvents are used to absorb such gases and each of them has different physicochemical properties because of their molecular structures. In the absence of a complete structures and properties information, group contribution thermodynamic methods are applied. Therefore, this research aims to compare physicochemical properties of the methods proposed by Joback, Constantinou and Marrero methods. The results show that the best method is that of Marrero for aqueous amine solutions. The small error can be explained by the inclusion of more molecule information for this method when compared to the other ones.

Keywords: Absorption Solvent; Amines; Group Contribution; Comparison of Methods.

COMPARAÇÃO ENTRE PROPRIEDADES FÍSICO-QUÍMICAS PARA SOLVENTES DE AMINA POR MEIO DE MÉTODOS DE CONTRIBUIÇÃO DE GRUPOS

Resumo: Os compostos CO_2 e H_2S são gases ácidos (AG) conhecidos por afetar negativamente o meio ambiente devido ao seu potencial de corrosão. Como solução, os solventes de amina são usados para absorver esses gases e cada um deles tem diferentes propriedades físico-químicas devido às suas estruturas moleculares. Na ausência de uma estrutura completa e informações de propriedades, métodos termodinâmicos de contribuição de grupo são aplicados. Portanto, esta pesquisa tem como objetivo comparar propriedades físico-químicas dos métodos propostos por Joback, Gani e Marrero. Os resultados mostram que o melhor método é o de Marrero para soluções aquosas de aminas. O pequeno erro pode ser explicado pela inclusão de mais informações da molécula para este método quando comparado aos outros.

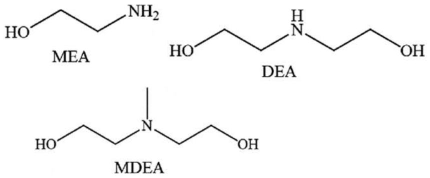
Palavras-chave: Solvente de Absorção; Aminas; Contribuição do Grupo; Comparação de Métodos.

1. INTRODUCTION

Natural gas (NG) is a fossil energy that needs treatment before its final use due to the harmful potential of AG present in NG. These gases negatively impact the environment as a greenhouse gas (e.g.: CO_2) and gas production pipelines by corrosion (e.g.: hydrogen sulfide (H_2S)). Besides, to solve this problem an aqueous amine solution for AG absorption has been used being an important component in AG sweetening process over the years [1].

The conventional amine solvents are monoethanolamine (MEA), ethyl diethanolamine (DEA), triethanolamine (TEA), diethylene glycol amine (DGA), diisopropanolamine (DIPA) and methyl diethanolamine (MDEA). Some of these structures are illustrated in the Figure 1. These are differentiated by the amine type such as primary (R_1NH), secondary (R_1R_2NH) and tertiary (R_1R_2 R_3N). These amine types directly influence absorption capacity and rate, and AG selective [2,3].

Figure 1. Conventional Amine Solvents Structures.



Source: NAKAO, Shin-ichi *et al*. Advanced CO2 Capture Technologies. (2019)

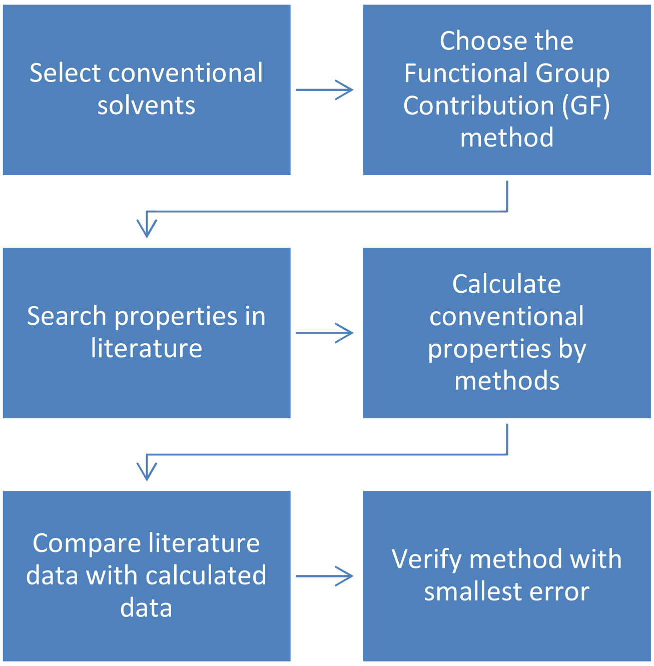
To achieve a desirable process efficiency, the compound structure must generate advantageous physicochemical properties such as: pH, surface tension, density, viscosity, etc. Furthermore, AG reactivity depends on the solvent chemical structure. For this reason, more functional group studies are necessary to improve AG cleaning processes. Usually, thermodynamics models predict molecular properties through functional groups such as UNIFAC [4,5].

There is a large volume of published studies proposing functional group contribution methods. The first one was proposed in 1955 by Lydersen [6] which was developed to describe properties such as critical pressure, volume, and temperature. Since then, most methods have been developed based on it. One example is the method of Joback & Reid [9] which describes eight more physicochemical properties than Lydersen approach. Furthermore, this method introduces new parameters for critical properties determination [8,9]. Furthermore, Constantinou & Gani [11,12] method presents two group contribution types in the molecule: first-order group which express individual functional group, and second-order group that relate functional groups blends.

Each group contribution method has a different accuracy depending on the molecular structure category [8,10]. Thus, this study aims to investigate the differences between group contribution method of Joback & Reid [9], Gani & Constantinou [11,12], and Marrero & Gani [13] for amine-based solvents. Thus, the result of this study will identify the best method for describing the physicochemical properties of amine solvents. These selected methods can be used to determine property values not reported in the literature and to aid the development of new compounds as amine solvents.

2. METHODOLOGY

Figure 2. Methodology Steps.



Source: Author's own elaboration.

The steps of this study are described in the Figure 2. Initially, three group contribution methods were chosen. As mentioned earlier, these methods are Joback & Reid, Gani & Constantinou, and Marrero & Gani [9,11,12,13]. Subsequently, conventional amine solvents were taken according to a previous literature investigation. Following the chosen methods, all the calculations were performed using Microsoft Excel™ spreadsheet software. After the properties calculations, the compounds constant data were collected from ChemSpider [14], Webbook NIST [15], PubChem [16] and DIPPR 801 [17] databases.

To study the properties was chosen only the equally known properties in each method and only for experimental data. These properties are melting temperature (T_m) in K, boiling temperature (T_b) in K, critical temperature (T_c) in K, critical pressure (P_c) in bar and critical volume (V_C) in cm^3/mol. To verify the methods was apply relative deviation (RD) (Eq. (1)) for each compound (i), average (A) (Eq. (2)) for each property (j) and average (Eq. (3)) of A for each method. The lowest error result is the most appropriate group contribution method for amine solvents properties prediction. Finally, all results were analyzed and discussed.

$$RD_i = \frac{|x_{Calculated} - x_{Data}|}{x_{Data}} \times 100 \tag{1}$$

$$A_j = \frac{\sum_{i=1}^{n} RD_i}{n} \tag{2}$$

$$Error = \frac{\sum_{j=1}^{n} A_j}{n} \tag{3}$$

3. RESULTS AND DISCUSSION

The chosen solvents are MEA, DEA, TEA, DGA, DIPA, MDEA, triethylenetetramine (TETA), diethylenetriamine (DETA) and piperazine (Pz) following previous works [18,19,20]. Table 1 shows the literature experimental results. Subsequently, select properties were calculated and the results were compared with experimental, as shown in Table 2, Table 3, and Table 4.

Table 1. Properties of Literature [14,15,16,17].

Solvent	Formula	T_m [K]	T_b [K]	T_c [K]	P_c [bar]
MEA	C_2H_7NO	283.150	443.150	678.200	71.240
DEA	$C_4H_{11}NO_2$	301.150	541.150	736.600	42.700
TEA	$C_6H_{15}NO_3$	292.150	463.150	772.100	27.430
DGA	$C_4H_{11}NO_2$	262.150	491.150	675.706	37.188
DIPA	$C_6H_{15}NO_2$	311.150	522.150	672.000	36.000
MDEA	$C_5H_{13}NO_2$	252.150	519.150	675.000	38.800
TETA	$C_6H_{18}N_4$	238.150	540.150	718.000	31.700
DETA	$C_4H_{13}N_3$	233.150	472.150	677.000	42.200
Pz	$C_4H_{10}N_2$	381.150	419.150	661.000	58.000

Table 2. Joback & Reid Relative Deviation.

Solvent	Formula	T_m [K]	T_b [K]	T_c [K]	P_c [bar]
MEA	C_2H_7NO	9.45%	7.46%	13.24%	11.72%
DEA	$C_4H_{11}NO_2$	2.65%	2.86%	6.63%	18.64%
TEA	$C_6H_{15}NO_3$	27.44%	35.13%	1.33%	399.87%
DGA	$C_4H_{11}NO_2$	14.88%	2.63%	3.27%	24.44%
DIPA	$C_6H_{15}NO_2$	3.04%	9.27%	9.64%	11.13%
MDEA	$C_5H_{13}NO_2$	19.06%	1.61%	1.07%	256.72%
TETA	$C_6H_{18}N_4$	80.23%	7.80%	8.36%	15.31%
DETA	$C_4H_{13}N_3$	51.84%	3.01%	1.37%	8.92%
Pz	$C_4H_{10}N_2$	6.46%	1.60%	3.01%	0.14%

Table 3. Constantinou & Gani Relative Deviation.

Compound	Formula	T_m [K]	T_b [K]	T_c [K]	P_c [bar]

MEA	C_2H_7NO	4.35%	2.01%	8.39%	14.88%
DEA	$C_4H_{11}NO_2$	5.64%	6.76%	9.05%	3.80%
TEA	$C_6H_{15}NO_3$	1.99%	20.87%	7.23%	26.29%
DGA	$C_4H_{11}NO_2$	3.90%	4.82%	4.73%	16.81%
DIPA	$C_6H_{15}NO_2$	4.75%	1.81%	4.07%	1.10%
MDEA	$C_5H_{13}NO_2$	7.69%	0.98%	0.69%	5.60%
TETA	$C_6H_{18}N_4$	42.55%	1.81%	0.19%	17.12%
DETA	$C_4H_{13}N_3$	32.74%	0.92%	2.46%	13.98%
Pz	$C_4H_{10}N_2$	22.81%	0.06%	4.16%	0.60%

Table 4. Marrero & Gani Relative Deviation.

Compound	Formula	Tm [K]	Tb [K]	Tc [K]	Pc [bar]
MEA	C_2H_7NO	4.03%	9.36%	8.29%	6.67%
DEA	$C_4H_{11}NO_2$	1.99%	7.63%	9.83%	2.62%
TEA	$C_6H_{15}NO_3$	14.10%	22.10%	4.22%	21.49%
DGA	$C_4H_{11}NO_2$	8.19%	2.30%	2.03%	17.75%
DIPA	$C_6H_{15}NO_2$	7.91%	3.43%	6.64%	8.33%
MDEA	$C_5H_{13}NO_2$	17.56%	2.72%	0.47%	2.15%
TETA	$C_6H_{18}N_4$	19.77%	0.32%	1.23%	2.42%
DETA	$C_4H_{13}N_3$	20.62%	0.41%	1.92%	0.16%
Pz	$C_4H_{10}N_2$	13.97%	7.82%	3.86%	3.18%

The Tables 2, 3 and 4 show a deviation between 0.06% and 399.87%. These results designate a large variation in those deviation values, because of the heterogeneity aspects of the evaluated methods' according to each molecular structure. This is an indication that a broader analysis is required. For this purpose, it was carried out a mean calculation for each property, as exhibited in Table 5 where the results for Joback & Reid [9], Constantinou & Gani [11,12] and Marrero & Gani [13] were 30.03%, 8.55% and 7.43%, respectively. It reveals a higher deviation (30%) for all the properties evaluated by Joback & Reid [9] method. Though, it was expected once a non-consideration of functional groups interaction results in a value that is far from reality. The other two Gani methods indicate a deviation lower than a third of Joback & Reid's [9], despite of a difference less than 2% between Constantinou and Marrero [13] methods.

Marrero [13] predicts a better performance for all the properties showed in Table 5, except for the boiling temperature. A possible explanation for this might be that deviation results depend on the selected structures and the number of analyzed compounds. In other words, the more compounds analyzed, the better the accuracy of the results. A better performance of Marrero [13] may be explained by the third-order groups that add others molecular structures relations, in addition to what was described in second-order groups [13].

Table 5. Calculation of Error Method.

Method	T_m [K]	T_b [K]	T_c [K]	P_c [bar]	Relative Deviation
Joback & Reid [8]	23.90%	7.93%	5.32%	82.99%	30.03%
Constantinou & Gani [10,11]	14.05%	4.45%	4.55%	11.13%	8.55%
Marrero & Gani [12]	12.02%	6.23%	4.28%	7.20%	7.43%

4. CONCLUSION

This paper addressed a study to determine a group contribution method with higher accuracy. After the analysis, it was found that the best method is the one proposed by Marrero & Gani with 7.43% relative deviation. However, this result can be improved, becoming accurate. For this case, it would be necessary adding more compounds or following another strategy for property prediction methods investigation. The research has also shown that, the more the molecule is represented, the more suitable is the method is for predicting the properties of that molecule.

Acknowledgments

I wish to show my gratitude to PRH (Human Resources Program) 27.1 of the ANP and FINEP for the opportunity to develop the research with the financial support.

5. REFERENCES (ARIAL 12)

[1] NAJI, Samah Zaki; ABD, Ammar Ali. Sensitivity analysis of using diethanolamine instead of methyldiethanolamine solution for GASCO'S Habshan acid gases removal plant. **Frontiers in Energy**, v. 13, n. 2, p. 317-324, 2019.

[2] LEE, Woo Yun *et al*. Simultaneous removal of CO2 and H2S from biogas by blending amine absorbents: a performance comparison study. **Energy & Fuels**, v. 34, n. 2, p. 1992-2000, 2020.

[3] NARKU-TETTEH, Jessica *et al*. Effect of side chain structure and number of hydroxyl groups of primary, secondary and tertiary amines on their post-combustion CO2 capture performance. **Energy Procedia**, v. 114, p. 1811-1827, 2017.

[4] ADEYEMI, Idowu; ABU-ZAHRA, Mohammad RM; ALNASHEF, Inas M. Physicochemical properties of alkanolamine-choline chloride deep eutectic solvents: Measurements, group contribution and artificial intelligence prediction techniques. **Journal of Molecular Liquids**, v. 256, p. 581-590, 2018.

[5] NOROOZI, Javad; SMITH, William R. Accurately Predicting CO2 Reactive Absorption Properties in Aqueous Alkanolamine Solutions by Molecular Simulation Requiring No Solvent Experimental Data. **Industrial & Engineering Chemistry Research**, v. 59, n. 40, p. 18254-18268, 2020.

[6] LYDERSEN, A. L. Estimation of critical properties of organic compounds. **Univ. Wisconsin Coll. Eng., Eng. Exp. Stn. Rep. 3**, 1955.

[7] NAKAO, Shin-ichi *et al*. Chemistry of Amine-Based CO 2 Capture. In: **Advanced CO2 Capture Technologies**. Springer, Cham, 2019. p. 3-22.

[8] POLING, Bruce E.; PRAUSNITZ, John M.; O'CONNELL, John P. **Properties of gases and liquids**. McGraw-Hill Education, 2001.

[9] JOBACK, Kevin G.; REID, Robert C. Estimation of pure-component properties from group-contributions. **Chemical Engineering Communications**, v. 57, n. 1-6, p. 233-243, 1987.

[10] STEFANIS, Emmanuel; CONSTANTINOU, Leonidas; PANAYIOTOU, Costas. A group-contribution method for predicting pure component properties of biochemical and safety interest. **Industrial & engineering chemistry research**, v. 43, n. 19, p. 6253-6261, 2004.

[11] CONSTANTINOU, Leonidas; GANI, Rafiqul. New group contribution method for estimating properties of pure compounds. **AIChE Journal**, v. 40, n. 10, p. 1697-1710, 1994.

[12] CONSTANTINOU, Leonidas; GANI, Rafiqul; O'CONNELL, John P. Estimation of the acentric factor and the liquid molar volume at 298 K using a new group contribution method. **Fluid Phase Equilibria**, v. 103, n. 1, p. 11-22, 1995.

[13] MARRERO, Jorge; GANI, Rafiqul. Group-contribution based estimation of pure component properties. **Fluid Phase Equilibria**, v. 183, p. 183-208, 2001.

Available from: <full address>. Accessed on: day, month and year

[14] ROYAL SOCIETY OF CHEMISTRY. **ChemSpider**, 2021. Available from: <www.chemspider.com>. Accessed on: July 19, 2021.

[15] National Institute of Standards and Technology. **Webbook NIST**, 2018. Available from: <webbook.nist.gov>. Accessed on: July, 2021.

[16] National Library of Medicine. **PubChem**, 2021. Available from: <pubchem.ncbi.nlm.nih.gov>. Accessed on: July 23, 2021.

[17] BLOXHAM, Joseph C. et al. Proper use of the DIPPR 801 database for creation of models, methods, and processes. **Journal of Chemical & Engineering Data**, v. 66, n. 1, p. 3-10, 2020.

[18] ESMAEILI, Arash *et al*. Assessment of carbon dioxide separation by amine solutions using electrolyte non-random two-liquid and Peng-Robinson models: Carbon dioxide absorption efficiency. **Journal of Construction Materials**, v. 2, p. 3-10, 2021.

[19] ARACHCHIGE, Udara SPR. Amines' effect on CO2 removal efficiency. 2019.

[20] ZHAO, Wenbo *et al*. Liquid-solid phase-change absorption of acidic gas by polyamine in nonaqueous organic solvent. **Fuel**, v. 209, p. 69-75, 2017.