VISCOSITY OF POTASSIUM CARBONATE SOLUTIONS PROMOTED BY NEW AMINES

MARIA HARJA, ELISABETA HULTUANĂ, NICOLAE APOSTOLESCU, GABRIELA ANTOANETA APOSTOLESCU, RAMONA-ELENA TĂTARU – FĂRMUȘ*

Universitatea Tehnică „Gheorghe Asachi" din Iaşi, România

Abstract. The objective of this paper is presenting the experimental results of the viscosity measuring for the aqueous solutions of potassium carbonate with new amines as promoters. In this work, ethylenediamine (EDA) and triethylenetetramine (TETA) were chosen as rate promoter candidates. The viscosity of the ternary aqueous solutions (K2CO3-Amine-H2O) has been measured for a blending 25 wt % potassium carbonate, amine concentrations between 1 to 7 wt % for EDA and 1 to 3 % for TETA, at atmospheric pressure and temperatures from 298 K to 343 K.

Key words: ethylenediamine, triethylenetetramine, potassium carbonate, promoters, viscosity.

1. Introduction

Post-combustion separation and capture of carbon dioxide (CO_2) from gaseous is a challenging technique due to low pressure and low carbon dioxide concentration, the presence of impurities in combustion gases and the cost of the regeneration of the absorber. CO_2 can be captured by a wide variety of techniques, such as absorption in amine solutions, membrane separation, cryogenic separation, etc. [1]. In accordance with current technologies, only absorption and some membranes are considered to be economically viable. Researches offer ample studies to reactive absorption (chemisorption), enhanced by the presence of a rapid reaction in the [1-3]. A lot of solvents have been applied to gas treating, but the most effective are generally considered to be aqueous amines or hot potassium carbonate (hotpot) solvents.

---

*Correspondence address: tframona@yahoo.com

Articles published in recent years indicate researchers' efforts to find new CO_2 absorbers [4]. The choice of solvent takes into account the following properties: gas solubility; volatility, corrosivity, cost, viscosity, chemical stability, toxicity, low freezing point etc.

Potassium carbonate (K_2CO_3) solution is a widely used solvent for CO_2 removal due to the low toxicity, low tendency of degradation, less energy requirement, high solubility in the carbonate / bicarbonate system and other economic concerns like corrosion problem [4]. For absorption, an aqueous solution of 20-40% K_2CO_3 is used as close as possible to the saturation without the phenomenon of crystallization.

Since the rate of CO_2 absorption is relatively slow in K_2CO_3, different promoters (activators) have been required [1, 2]. Research on the absorption of CO_2 in K_2CO_3 solutions with amines was initiated in 1967 by Danckwerts and McNeil [3]. Primary and secondary amines are commonly used as promoters in potassium carbonate solutions, while tertiary amines are rarely used as promoters because they do not have a significant accelerating effect [3, 4]. The most commonly used amines in the literature are monoethanolamine (MEA), diethanolamine (DEA) and piperazine (PZ) [6-8]. Also, diglyolamine (DGA), methyl diethanolamine (MDEA), 2-ethylaminoethanol (EAE), diisopropanolamine, methyl-amino ethanol (MAE) etc., can be used. Although some of the amines are already used in the absorption processes as activators, studies need to be expanded to elucidate less well-known aspects.

Prior to the experimental determinations specific to the absorption process, all the physical properties of aqueous solutions involved must be known: the viscosity and density of the solution, the CO_2 diffusion coefficient in the real solution, as well as the Henry constant for CO_2 etc.

The present work belongs to a research project aimed to find a new promoter for potassium carbonate aqueous solutions, used as solvent for carbon dioxide absorption. Two amines take into consideration: ethylenediamine (EDA)- a primary diamine and triethylenetetramine (TETA)- a tetramine with 2 primary groups and 2 secondary groups. Based on the accumulated experience [9-11] and previous research, these amines have potential for promotion. Previous experimental results led to the conclusion that TETA is superior to MEA from a kinetic point of view [9-13]. Few amines (PZ only) exceed MEA at the absorption rate.

2. Experimental

2.1. Materials

Chemicals were used as received unless otherwise stated. Potassium carbonate 99 % was provided from Fluka Analytical. Ethylenediamine (EDA) was purchased from Aldrich with a certified GC purity greater than 99%. Tetraethylenetetramine (TETA) was purchased from Across Organics with a purity of 99.5%. The main properties of the two investigated amines are presented in the table 1.

Table 1. **Properties of the studied amines**

Property	EDA	TETA
Chemical formula	$C_2H_8N_2$	$C_6H_{18}N_4$
Molecular weight, kg/ kmol	60.10	146.24
Density, at 293 K, kg/m^3	897	974
Viscosity, at 293 K, mPa s	1.8	26.0
Vapor pressure, at 293 K, mmHg	10.40	< 0.01
Refractive index, at 293 K	1.457	1.499
pH of 1% wt solution	11.7	11.5

The water came from an apparatus delivering ultra pure water (Millipore). The solutions have been prepared gravimetrically (% wt) under the vacuum. Each of the solutions contains 25 wt. % of potassium carbonate and amine between 1 and 7 % wt. (EDA) and 1 to 3 % wt. (TETA), at temperatures between 298 K and 343 K.

2.2. Experimental methods

A SP-870 plus METERTECH UV–Vis spectrophotometer was used to monitor the K_2CO_3-EDA/TETA systems, and to plot the diagram of absorbance, optical path =1cm. The viscosity was measured with an Ostwald type viscometer. Water was used as calibrating liquid. The temperature was controlled within ± 0, 1 K in a water bath. A standard chronometer was employed for the time flowing measuring (12 times for each probe) with an accuracy of 0.01 s. The maximum error of viscosity measuring was estimated at ±1, 00 %.The details of the methods and techniques used to determine η have been described previously [10].

3. Results and discussion

3.1. Absorbance

The UV-Vis spectra were recorded for EDA, TETA and K_2CO_3 as well as for K_2CO_3 (25%) + EDA (3, 5, 7 %) and K_2CO_3 (25%) + TETA (3, 5%). All the spectra are similar, exhibiting a maximum absorption in the UV-A range (320-390 nm) (Fig. 1 and Fig. 2). The high absorption maximum for 330 nm in mixtures is most likely due to the formation of hydrogen bonds between the hydrogen atoms bonded covalently to the amine chain and the oxygen atoms in K_2CO_3 [14]. Compared to the spectrum of potassium carbonate, the hyperchromic effect can be observed. It increases with increasing amine concentration, for all the mixture.

3.2. Viscosity

It is presumed that the viscosity of absorbents can affect the CO_2 absorption rate. Solvents with low viscosity can increase the diffusion coefficient of CO_2 in the liquid phase, which results in a low mass transfer resistance [145

The measured viscosity results for aqueous blends of K_2CO_3-TETA-H_2O at different concentrations and temperatures are given in Fig. 3. At higher values for TETA concentration (higher than 3 %), the two components (the potassium carbonate solution and TETA solution) are delimited. Experimental determinations of the viscosity of the system K_2CO_3-TETA-H_2O allowed only 2 concentrations (1% and 3% TETA); with reproducible results.

The experimental results for K_2CO_3-EDA-H_2O are presented in the Fig. 4, for 25 % K_2CO_3 and different mass concentrations of EDA (1 to 7 % wt.). To convert % wt. into molar concentrations the experimental densities of these solutions have been used. The viscosity continuously increases with concentration and decreases with temperature, for each system, as expected. This could be due to a decrease in the internal resistance of the molecules with increasing temperature, which allows the solution molecules to flow easily, thereby reducing the viscosity. However, with increasing concentration of EDA or TETA in the aqueous solutions of potassium carbonate, the viscosity tended to increase. The higher concentrated solutions had a higher viscosity than the lower ones, which may be due to the increased molecular resistance in the more concentrated solutions.

There is a rich collection of data that quantifies the viscosity of aqueous electrolyte solutions, including K_2CO_3. Experimental data include a wide variety of conditions (carbonate concentration, bicarbonate concentration, amine concentration temperature, etc.) [16-20]. In literature are presented complex group contribution methods or matrix calculations to express viscosity [19-25]. Although data are available, the correlation of the viscosity values of potassium carbonate with activators solutions is difficult because the properties of the liquid vary greatly in composition and temperature. Therefore, a new empirical polynomial equation (1) was confronted with the experimental data:

$$\eta = a\,C^2 + b\,C + d \qquad (1)$$

where η is the viscosities of the 2.27 mol/L K_2CO_3 + X mol/L EDA solution, and C is the molar concentration of EDA (mol/L). The coefficients a, b, d of the equation have been identified for each system and for each temperature. The optimized values of the coefficients a, b, and d of the equation (1) are tabulated (Table 2).

Table 2. The coefficients a, b, d
at different temperatures for K_2CO_3-EDA-H_2O system

Temperature, K	K_2CO_3-EDA-H_2O $\eta = aC^2+bC+d$		
	a	b	d
298	1.0522	-0.9922	4.1613
303	0.6778	-0.588	3.4436
313	0.3753	-0.1873	2.3085
323	0.1101	0.0517	1.6184
333	0.1616	-0.1508	1.2808
343	0.0954	-0.0329	0.9559

The experimental viscosities for the potassium carbonate - EDA solutions are compared with calculated results in fig. 5. The identified values of the coefficients a, b, d verify the experimental points with deviations not exceeding 2 %.

Results obtained are in accordance with literature data [25] and demonstrated that proposed amines have properties comparatively with other amines.
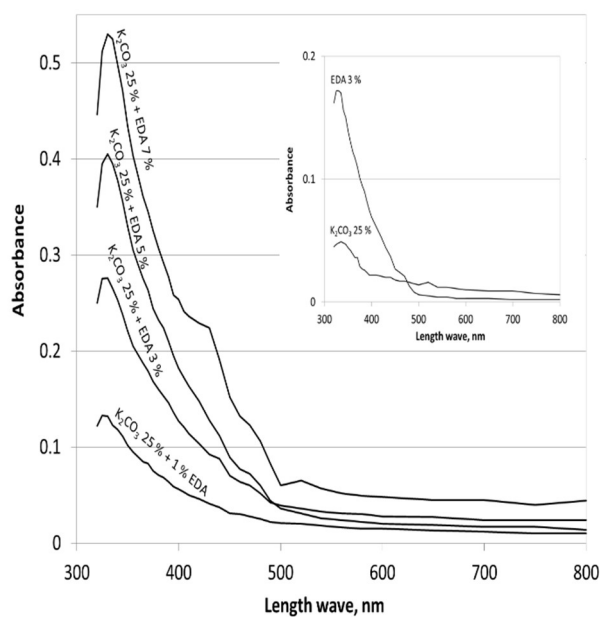

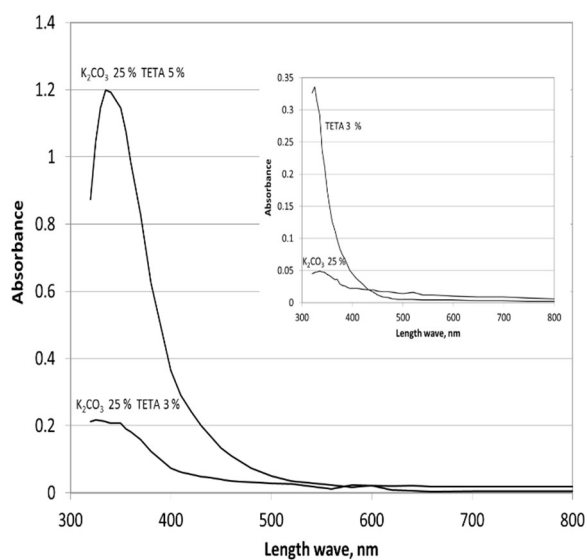Fig. 1. The UV-Vis spectra for EDA, K_2CO_3 and K_2CO_3 (25%) + EDA (3, 5, 7 %)

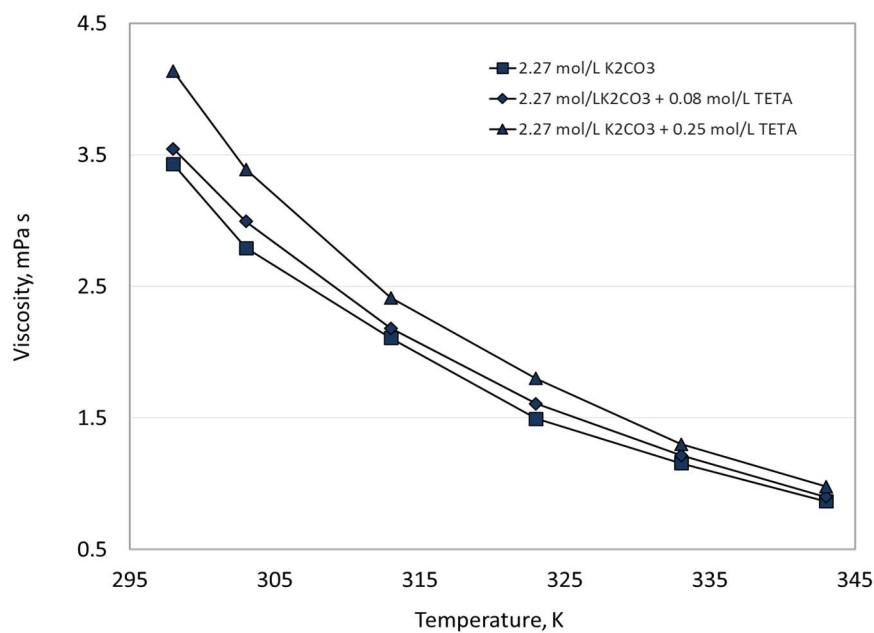Fig. 2. The UV-Vis spectra for TETA, K_2CO_3 and K_2CO_3 (25%) + TETA (3, 5 %)

Fig. 3. Viscosity for aqueous blends of K_2CO_3+TETA at different concentrations and temperatures
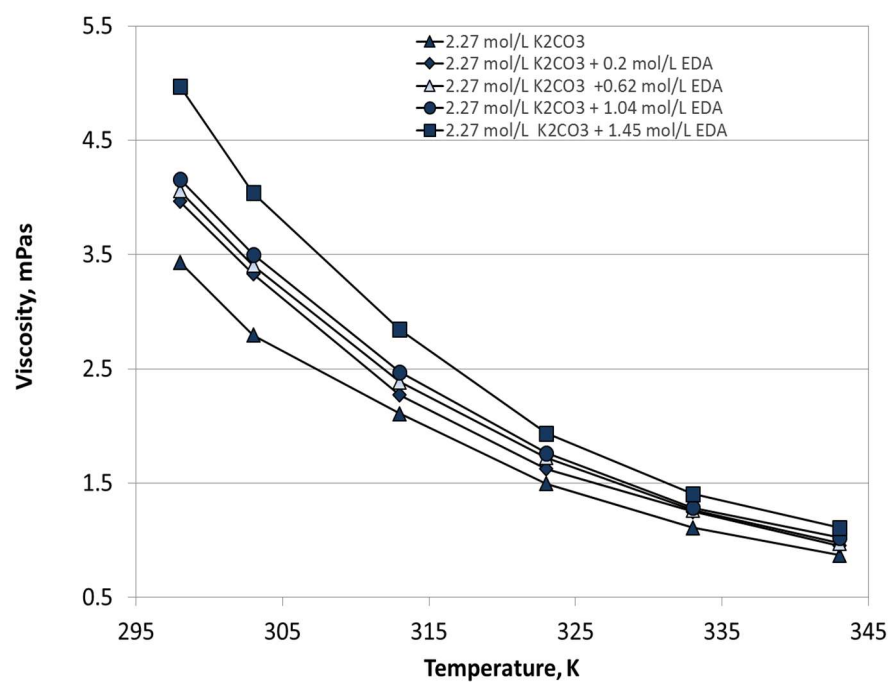

Fig. 4. Viscosity for aqueous blends of K_2CO_3+EDA at different concentrations and temperatures
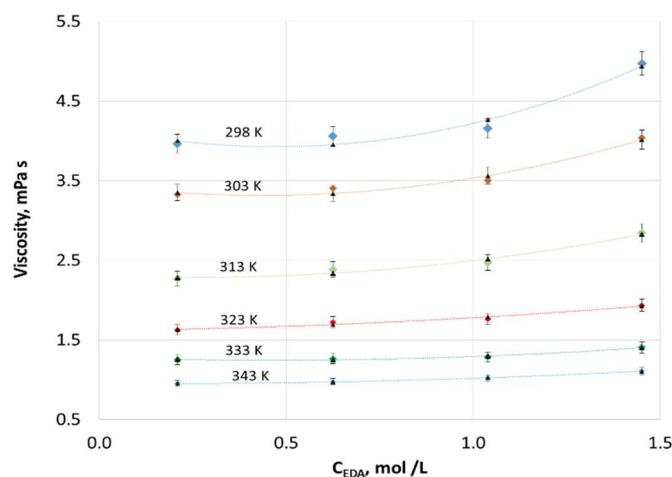
Fig. 5. Experimental and calculated viscosity variation, with EDA concentration and temperature

5. Conclusions

The viscosities of aqueous solutions of potassium carbonate + ethylenediamine (EDA) and potassium carbonate + triethylenetetramine (TETA) have been measured in the concentration range of 25 wt % potassium carbonate and amine between 1 and 7 % wt. (EDA) and 1 to 3 % wt. (TETA), at temperatures between 298 K and 343 K. Experimental determinations allowed only 2 concentrations for the aqueous system K_2CO_3+TETA (1% and 3% TETA). At higher amine concentration values, the two components (the potassium carbonate solution and TETA solution) are strictly delimited.

The experimental data obtained to determine the viscosity of the K_2CO_3+EDA+H_2O system were correlated with a polynomial equation with three coefficients, depending on the temperature and concentration of the amine.

The results are useful for the prediction other properties of the studied solutions necessary in carbon dioxide absorption in promoted potassium carbonate solutions.

Validated equation will be used for modeling of the reactor; corrected value used in reactor model is essential.

References
[1]   Guo, D., Thee, H., Tan C.Y., Chen, J., Fei, W., Kentish, S., Stevens, G., da Silva, G., *Amino Acids as Carbon Capture Solvents: Chemical Kinetics and Mechanism of the Glycine + CO_2 Reaction,* Energy Fuels, **277**, 2013, p. 3898-3904.
[2]   Thee, H., Smith, K.H., Silva, G.D., Kentish, S.E., Stevens, G. W., *Carbon dioxide absorption into unpromoted and borate-catalyzed potassium carbonate solutions*, Chem. Eng. J., vol. s **181–182**, 2012, p. 694–701.

[3]   Danckwerts, P.V., Mcneil, K.M., *The effects of catalysis on rates of absorption of CO2 into aqueous amine—potash solutions*, Chem. Eng. Sci., **22**, 1967, p. 925–930.

[4]   Harja, M., Ciobanu, G., Juzsakova, T., Cretescu, I. *New Approaches in Modeling and Simulation of CO2 Absorption Reactor by Activated Potassium Carbonate Solution*. Processes, **7,** 2, 2019, p. 78.

[5]   Versteeg, G.F., van Dick, L.A.J., van Swaaij, P.M., *On the kinetics between CO_2 and alkanolamines both in aqueous and non-aqueous solutions. An overview*, Chem. Eng. Commun., **144,** 1996, p. 113–158.

[6]   Behr, P., Tunnat, A., Maun, A., Gorner, K., *Optimization of CO_2 Capture from Flue Gas with Promoted Potassium Carbonate Solutions*, Energy Procedia, **37**, 2013, p.1554–1565.

[7]   Borhani, T.N.G., Akbari, V., Hamid, M. K. A., Manan, Z.A., *Rate-based simulation and comparison of various promoters for CO_2 capture in industrial DEA-promoted potassium carbonate absorption unit*, J. Ind. Eng. Chem. **22**, 2015, p. 306–316.

[8]   Heischkamp, E., Varlik, M., Korkmaz Ö., Oeljeklaus, G., Görner, K., *Analysis of operating conditions of a flue gas scrubbing process for CO2 separation in a coal-fired power plant*, Energy Procedia, **4**, 2011 1377–1384.

[9]   Tataru- Farmus, R.E., *Studiul absorbţiei CO_2 în noi soluţii de amine*, Teză de doctorat, Universitatea Tehnică Gheorghe Asachi din Iași, 2011.

[10]   Tataru- Farmus, R.E., Siminiceanu, I., Bouallou, Ch., *Carbon dioxide absorption into new formulated amine solutions* (I), Chemical Engineering Transactions, **12**, 2007, p. 175- 181.

[11]   Siminiceanu, I., Tataru-Farmus, R.E., Amann, J.-M., *Kinetics of carbon dioxide absorption into aqueous solutions of etilenediamine*, Buletinul Inst. Polit. Iasi, Tome **52(56),** 1-2, Chim si Ing. Chim., 2006, p. 45- 50.

[12]   Hu, G., *Novel promoters for carbon dioxide absorption in potassium carbonate solutions*, 2018, Doctoral dissertation, Melbourne School of Engineering, The University of Melbourne, Australia

[13]   Harja, M.; Ciobanu, G.; Rusu, L.; Lazăr, L., *Effectiveness factor approach for chemical absorption process,* Env. Eng. Manag. J., **17**, 4, 2018, p. 813-820.

[14]   Ünveren, E.E., Monkul, B.O., Sarıoğlan, Ş., Karademir, N., Alper,E., *Solid amine sorbents for CO2 capture by chemical adsorption: A review*, Petroleum, **3**, 1, 2017, p. 37-50.

[15]   Shen, Sh., Yang, Y., Wang, Y., Ren, Sh., Han, J., Chen, A., *CO_2 absorption into aqueous potassium salts of lysine and proline: density, viscosity and solubility of CO_2.* Fluid Phase Equilib., **399**, 2015, p. 40–49.

[16]   Bates, S. J., Baxter, W. P., *International Critical Tables of Numerical Data*, *Physics, Chemistry and Technology*. New York, McGraw-Hill, 1929.

[17]   Bocard, J.P., Mayland, B.J., *New Charts for Hot Carbonate Process*, Hydrocarbon Processing and Petroleum Refiner, **41**, 4, 1962, p. 128-132.

[18]   Goncalves, F.A., Kestin, J., *The Viscosity of Na_2CO_3 and K_2CO_3 Aqueous Solutions in the Range 20-60ºC*, Int. J. Thermophys. **2**, 4, 1981, p. 315-322.

[19]   Moniuk, W., Pohorecki, R., *Viscosity and Density of Sodium and Potassium Alkaline Solutions*, Hungarian J. Ind. Chem. Veszprem, **19**, 1991, p.175-178.

[20]   Vazquez, P.G., Chenlo, F., Moreira, R., Pardo, P., *Viscosity of the Following Na_2CO_3, $NaHCO_3$, $K2CO_3$, $KHCO_3$, Na_2CO_3-$NaHCO_3$, and K_2CO_3-$KHCO_3$ Solutions Important in Absorption Processes*, Afinidad Li May-June, 1994, p. 211-216.

[21]   Jiang, J.; Sandler, S.I., *A new model for the viscosity of electrolyte solutions*, Ind. Eng. Chem. Res., **42**, 2003, p. 6267-6272.

[22]   Tataru- Farmus, R.E., Siminiceanu, I., Bouallou, Ch., *Carbon dioxide absorption into new formulated amine solutions* (I), Chemical Engineering Transactions, **12**, 2007, p. 175- 181.

[23]   Jones, G., Dole, M., *The viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride*, J. Am. Chem. Soc., **51**, 1929, p. 2950- 2958

[24]   Bohloul, M.R., Sadeghabadi, M.A., Peyghambarzadeh, S.M., Dehghani, M.R., *CO_2 absorption using aqueous solution of potassium carbonate: Experimental measurement and thermodynamic modeling*, Fluid Phase Equilibria, **447**, 2017, p. 132-141.

[25]   Harja, M., Rusu, L., Barbuta, M., *The viscosity and density of the aqueous solutions used for the absorption accompanied by chemical reaction*, Bull. Pol. Inst. Iasi. Chem. Chem. Eng, **9**, 2008, p. 55- 62.