Carbon Dioxide Absorption Into New Formulated Amine Solution. (I)Solution Viscosity Measuring And Correlation

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The density and the viscosity of three binary aqueous solutions (A- H_2O) have been measured for amine concentrations between 0 and 20% w/w, and temperatures from 293 K to 333 K. These intervals could be of practical importance for the absorption of carbon dioxide from different gas mixtures. The three investigated amines were: ethylenediamine (EDA), tetraethylenetetramine (TETA) and N, N'-bis (3- aminopropyl) ethylenediamine (APEDA). The density and viscosity for each amine solution have been measured with an Anton Paar digital vibrating tube densimeter (DMA 5000 model) and an Ubbelohde type viscometer, respectively. The results on viscosity have been correlated with an empirical equation of the form: $Y = \eta/\eta_o = 1 + a C + b C^2 + d C^3$. The coefficients a, b, d of the equation have been identified for each system and each temperature.

Keywords: ethylenediamine, tetraethylenetetramine, N, N'-bis (3- aminopropyl) ethylenediamine, queous solutions, density, viscosity, measuring, correlation.

1. Introduction

Aqueous alkanolamine solutions are frequently used as solvents for removal of acidic gases such as carbon dioxide (CO_2) and hydrogen sulphide (H_2S) from gas streams in the natural gas, petroleum chemical plants, and ammonia industry. A wide variety of alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), di- isopropanolamine (DIPA), N- methyldiethanolamine (MDEA), 2- amino-2- methyl-1- propanol amine (AMP) have been used industrially for a number of years[1,2]. A recent advancement in gas treating technology is the application of *sterically hindered amines* which offer absorption capacity, absorption rate, selectivity, and degradation resistance advantages over conventional amines for CO_2 removal from gases [3]. The absorption of acid gases in *blended amines* has also important advantages over the use of single amines. The addition of a small amount of primary amine to conventional tertiary amines can enhance the absorption of CO_2 to a large extent without appreciably affecting the stripping characteristics. Blends of primary and tertiary amines, such as MDEA+ MEA + H_2O or AMP + MEA + H_2O have been studied as new attractive solvents for the acid gases treating processes [2]. The third direction for absorption improvement is the use of *formulated solvents* which are mixtures of basic amines, activators, antifoamers and corrosion inhibitors.
The present work belongs to a research project aimed to find a new formulated solvent for carbon dioxide absorption. Three new amines are taken into consideration:
. ethylenediamine (EDA),
. tetraethylenetetramine (TETA) and

. N, N$^{'}$-bis (3- aminopropyl) ethylenediamine (APEDA).

The main properties of the three investigated amines are presented in the table 1. Many essential properties of APEDA have not been found in the literature. The objective of this paper is to presents the experimental results of the viscosity and density measuring and their correlation, for the aqueous solutions of the three amines. Such data have not been found in published monographs and handbooks [1, 2, 9, 10] nor in specialized journals [3, 4, 5, 6, 7, 11, 12]. However, there has been a long history of investigating the viscosity of electrolyte solutions. *Jiang and Sandler* [7] cited *Grueneisen* as the first who observed experimentally that at very low concentrations the viscosity of the electrolyte solutions increased nonlinearly with concentration, regardless of the type of the system. This effect, named *Grueneisen effect*, is generally correlated as:

$$\eta/\eta_o = 1 + a \ (C)^{1/2} \qquad (1)$$

where η and η_o are the viscosities of the solution and the pure solvent, respectively; a is a positive constant, and C is the electrolyte molar concentration (mol/L). Later, *Falkenhagen* and *Vermon* [5] established a method of calculating the coefficient a starting from the Debye- Hueckel theory. The a coefficient is related to the interactions and the mobility of solute ions, and is always positive. However, the equation (1) is only valid for concentrations up to about 0.01 mol/L [7]. Then, *Jones and Dole* [4] proposed a more complete formula in order to extend the field of validity:

$$\eta/\eta_o = 1 + a \ (C)^{1/2} + b \ C \qquad (2)$$

where b is the result of interactions between the solvent and the solute ions, and may be either positive or negative depending on the degree of solvent structuring introduced by the ions. Usually a positive value of b is associated with structure- making (ordering) ions, whereas a negative value of b is associated with structure- breaking (disordering) ions. The Jones- Dole equation (2) can reasonably well describe the experimental data but it is usually valid only for concentrations of less 0.1 mol/L. For more concentrated solutions, extended Jones- Dole equations with empirical terms of higher order have been propose. Kaminsky [6], for instance, added a quadratic term containing an empirical constant d:

$$\eta/\eta_o = 1 + a \ (C)^{1/2} + b \ C + d \ C^2 \qquad (3)$$

Jiang and Sandler [7] developed a new model, with a more microscopic basis, using the concept of Helmholtz activation energy. They tested the new equation for concentrations up to 12.3 mol/L by comparing with the values from Kaminsky equation and found a good agreement. Lenka et al.[8] developed a more complex theoretical model for the viscosity of multicomponent electrolyte solutions which accurately predicted viscosity of aqueous solutions up to about 30 mol/l and temperatures up to 573 K.

There are also many empirical equations: a modified Arrhenius equation, Einstein equation, etc. For the compilation of older empirical equations, see the handbooks [9, 10]. Generally, the data on other amine aqueous systems [11, 12] have been correlated by empirical equations. The semi- empirical equation (3), which has only one pure empirical constant (d), has been used in a first round but it was not well verified: the constant a was

positive and sometimes negative. Therefore, a new empirical polynomial equation (4) was confronted with the experimental data.

$$Y = \eta/\eta_o = 1 + a\,C + b\,C^2 + d\,C^3 \qquad (4)$$

2. Experimental

Ethylenediamine (EDA) was purchased from Aldrich with a certified GC purity grater than 99%. TETA came from Alfa Aesar, with the same purity. APEDA was purchased from Across Organics with a purity of 99.5%. The water came from an apparatus delivering ultra pure water (Millipore). Amine and water were carefully degassed before use. The solutions have been prepared gravimetrically (% w/w) under the vacuum.

The apparatus used for density measurements was an Anton Paar digital vibrating tube densimeter (DMA 5000 model) with a certified precision of 0.01 kg/ m^3. The viscosity was measured with an Ubbelohde type viscometer. Water was used as calibrating liquid. The temperature was controlled within ± 0, 1 K with a Viscometer Thermostat 655. A standard chronometer was employed for the time flowing measuring (12 times for each probe). The maximum error of viscosity measuring was estimated at ±1, 00 %. Both density and viscosity were determined for solutions with concentrations between 0 and 20% w/w, and temperatures between 293 K and 333 K.

Table 1
Properties of the studied amines

Property	EDA	TETA	APEDA
Chemical formula	$C_2H_8N_2$	$C_6H_{18}N_4$	$C_8H_{22}N_4$
Molecular weight, kg/ kmol	60.10	146.24	174.29
Boiling point, ^{0}C	117	277	173
Melting point, ^{0}C	11	- 35	-1.5
Density, at 293 K, kg/m^3	897	974	952
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	1.491
Heat of formation, J/mol	-79,409.64	- 55,100.50	
Heat of vaporization, at 1 bar, J/mol	37,737.23	55,013.84	
Specific heat, at 298 K, kJ/kg K	2.842	2.633	
Thermal conductivity, at 293 K, W/m K	0.2566	1.881	
Ionization constant at 298 K	0.73×10^{-4}	0.63×10^{-4}	
pH of 1%$_w$ solution	11.7	11.5	
Surface tension, at 293 K, N/m	0.042	0.0222	

3. Results And Discussion

The experimental results are presented in the tables 2 to 4 under the form of $Y = \eta/\eta_o$ for different molar concentrations. To convert %w into molar concentrations the experimental densities have been used. The reduced viscosity Y continuously increases with concentration and decreases with temperature, for each system, as expected. The optimized values of the coefficients a, b, and d of the equation (3) are tabulated (Table 5). The experimental reduced viscosities for the three amine solutions are compared with calculated results in figures 1 to 3.

Table 2
Experimental Y= f(C, T) dependence for EDA solutions

% w	293		303		313		323		333	
	C, mol/L	Y, (-)	C mol/L	Y(-)	C mol/L	Y(-)	C mol/L	Y(-)	C mol/L	Y(-)
0	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000
5	0.829	1.103	0.827	1.095	0.823	1.082	0.820	1.078	0.816	1.048
10	1.657	1.301	1.651	1.280	1.645	1.241	1.637	1.195	1.627	1.124
15	2.482	1.488	2.473	1.428	2.462	1.382	2.449	1.318	2.435	1.227
20	3.306	2.316	3.292	2.096	3.277	1.929	3.259	1.584	3.239	1.414

Table 3
Experimental Y= f(C, T) dependence for TETA solutions

% w	293		303		313		323		333	
	C, mol/L	Y, (-)	C mol/L	Y(-)	C mol/L	Y(-)	C mol/L	Y(-)	C mol/L	Y(-)
0	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000
5	0.341	1.135	0.340	1.116	0.339	1.100	0.337	1.078	0.335	1.055
10	0.681	1.438	0.678	1.420	0.676	1.323	0.673	1.273	0.669	1.207
15	1.020	1.819	1.016	1.760	1.012	1.688	1.007	1.649	1.001	1.386
20	1.359	2.442	1.353	2.238	1.347	2.001	1.339	1.824	1.331	1.614

Table 4
Experimental Y= f(C, T) dependence for APEDA solutions

% w	293		303		313		323		333	
	C, mol/L	Y, (-)	C, mol/L	Y, (-)	C, mol/L	Y, (-)	C, mol/L	Y, (-)	C, mol/L	Y, (-)
0	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000
5	0.286	1.155	0.285	1.140	0.284	1.129	0.283	1.110	0.281	1.048
10	0.570	1.461	0.568	1.372	0.566	1.350	0.563	1.299	0.560	1.241
15	0.853	2.150	0.850	1.979	0.846	1.806	0.842	1.597	0.837	1.476
20	1.135	2.653	1.130	2.445	1.125	2.259	1.119	1.967	1.112	1.801

Table 5

The coefficients **a, b, d** from the equation $Y = 1 + aC + bC^2 + dC^3$ at different temperatures for the three amines

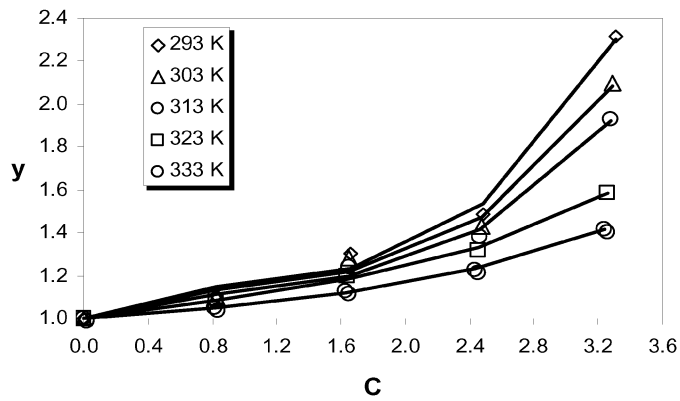| Amine Temperature, K	EDA			TETA			APEDA		
	a, L/mol	b, (L/mol)^2	d, (L/mol)^3	a, L/mol	b, (L/mol)^2	d, (L/mol)^3	a, L/mol	b, (L/mol)^2	d, (L/mol)^3
293	0.321	-0.240	0.079	0.303	0.347	0.154	-0.364	2.936	-1.166
303	0.278	-0.192	0.063	0.156	0.709	-0.111	-0.249	2.256	-0.792
313	0.220	-0.142	0.049	-0.075	1.112	-0.374	0.027	1.325	-0.311
323	0.126	-0.035	0.016	-0.314	1.617	-0.687	0.207	0.599	-0.009
333	0.063	-0.008	0.009	0.037	0.463	-0.109	-0.037	0.912	-0.209

Fig.1. Reduced viscosity of EDA- H_2O system (experimental: points; calculated: lines).

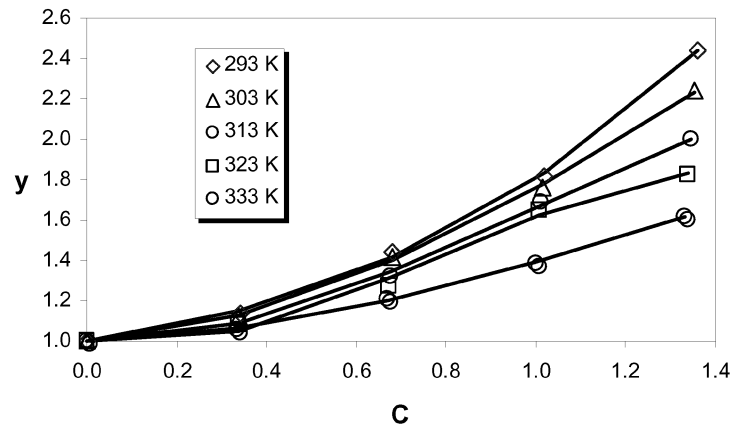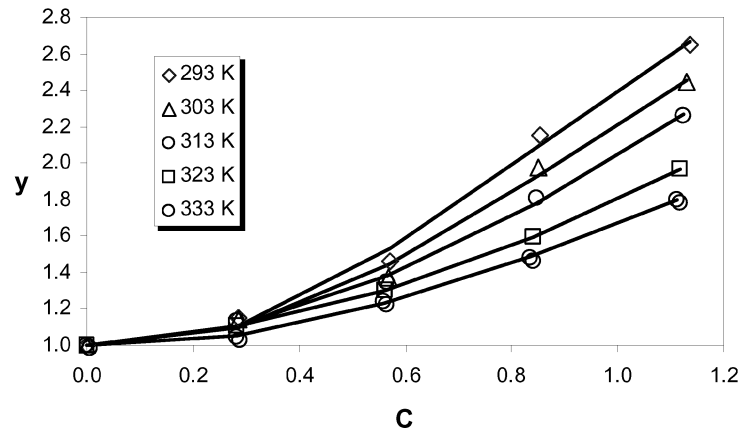*Fig.2. Reduced viscosity of TETA- H_2O system.*

Fig.3. Reduced viscosity of APEDA- H_2O system.

Table 6
The relative deviations (ε, %) of the equation (4) from experimental data.

Amine	%w	Temperature, K				
		293	303	313	323	333
EDA	5	-3.948	-3.614	-2.743	-0.924	-0.271
	10	5.049	4.669	3.675	1.234	0.436
	15	-2.997	-2.812	-2.180	-0.737	-0.298
	20	0.479	0.502	0.433	0.191	0.042

TETA	5	-1.297	-1.302	1.119	2.433	-0.485
	10	1.540	1.543	-1.404	-3.059	0.641
	15	-0.814	-0.834	0.738	1.634	-0.372
	20	0.152	0.165	-0.157	-0.322	0.086
APEDA	5	4.014	4.044	1.952	0.361	-0.823
	10	-4.793	-5.081	-2.472	-0.468	1.053
	15	2.187	2.367	1.243	0.256	-0.597
	20	-0.446	-0.483	-0.251	-0.052	0.124

Conclusions

. The densities and viscosities of aqueous solutions of ethylenediamine (EDA), tetraethylenetetramine (TETA), and N, N'-bis (3- aminopropyl) ethylenediamine (APEDA) have been measured in the concentration range from 0 to 20 %w/w and temperatures from 293 to 333 K.

. The viscosity data were correlated with concentration through an empirical equation with three coefficients which depend on the temperature and on the amine type. The deviations were up to 5.02%. The Kaminsky equation (3), despite its theoretical foundation, gave errors up to 35%.

. The equation is necessary for the prediction of carbon dioxide diffusion coefficients in such solutions.

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