

# ORTHOBARIC LIQUID DENSITY OF AQUEOUS BLENDED SOLVENTS AS A FUNCTION OF CONCENTRATION AND TEMPERATURE

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## ABSTRACT

This paper reports experimental values of density of aqueous mixtures of diethanolamine (DEA)+methyldiethanolamine (MDEA), DEA+2-amino-2-methy-1-propanol (AMP), DEA+2-piperidineethanol (2PE), DEA+N-methylpyrrolidone (NMP), MDEA+AMP, MDEA+NMP and NMP+AMP. The data were obtained at 313.15, 323.15, and 333.15 K, the total concentrations of the blended solvents studied were 30, 40 50 and 60 wt. %, for each total concentration at least 7 points were obtained with different proportions of each solvent, the estimated accuracy of the data is  $\pm 0.0002 \text{ g cm}^{-3}$ . From the density data molar excess volumes were derived, the information was correlated using the Redlich-Kister equation, the final expression includes the functionality of both concentration and temperature.

**KEY WORDS:** blended solvents; density; excess volumes; Redlich-Kister equation.

## 1. INTRODUCTION

Because of the extensive use of both aqueous solutions of blended alkanolamines and physical solvents blended with chemical solvents in gas sweetening applications, a complete knowledge of their thermophysical properties is of considerable interest.

In this work density data at 313.15, 333.15 and 323.15 K are reported for 7 solvent mixtures based on secondary diethanolamine (DEA), tertiary N-methyldiethanolamine (MDEA), hindered alkanolamines (2-amino-2-methyl-1-propanol AMP, 2-piperidineethanol 2PE) and in the physical solvent N-methylpyrrolidone (NMP). The ternary systems studied were: DEA+MDEA+H<sub>2</sub>O, DEA+AMP+H<sub>2</sub>O, DEA+2PE+H<sub>2</sub>O, DEA+NMP+H<sub>2</sub>O, MDEA+AMP+H<sub>2</sub>O, MDEA+NMP+H<sub>2</sub>O and NMP+AMP+H<sub>2</sub>O. The data were obtained at total solvent concentration of 30, 40 50 and 60 wt. %, and for a given total concentration at least 7 points were obtained varying the ratio of the solvents. From the density data excess volumes were derived and correlated with the well known Redlich-Kister equation.

The density for the pure components DEA, MDEA, AMP, 2PE and NMP, and for the binary systems DEA+H<sub>2</sub>O, MDEA+H<sub>2</sub>O, AMP+H<sub>2</sub>O, 2PE+H<sub>2</sub>O, and NMP+H<sub>2</sub>O at the temperatures and total concentration mentioned above is also included.

A review of the literature that reports density data for DEA, MDEA, AMP, 2PE, NMP, and aqueous solutions of one and two alkanolamines is given in table 1.

## 2. EXPERIMENTAL SECTION

The sample of DEA was obtained from Merck, MDEA, AMP and 2PE were obtained from Aldrich and the NMP from Fluka, all of them were purified by distillation using a

vacuum column and stored in molecular mesh. A chromatographic analysis of the distilled samples showed that the purity was always greater than 99 mol %, except for 2 PE that was 96 mol %.

Densities were measured with an Anton Paar DMA 45 Density Meter, which was calibrated with distilled water and ethylene glycol, making use of accurate values of density reported in the literature [1, 2]. The temperature was controlled within  $\pm 0.002\text{K}$  as measured with a Systemtechnik platinum resistance thermometer, the reproducibility of the measurements was  $5 \times 10^{-5} \text{ g cm}^{-3}$ , a Sartorius 2006 MP balance with a precision of  $\pm 0.0001 \text{ g}$  was used for mass measurements of aqueous solutions. A complete description of the experimental methodology has been described previously [3].

### **3. RESULTS AND DISCUSSION**

Table 2 shows the systems studied in this work. In table 3 the densities of pure DEA, MDEA, AMP, 2PE, NMP, are reported, also literature data are included, an absolute average deviation (AAD) of  $\pm 0.001 \text{ g cm}^{-3}$  was obtained.

The experimental densities values for MDEA-H<sub>2</sub>O at 313.15 K in the whole range of concentration and for the aqueous mixtures of DEA-MDEA and DEA-AMP at 313.15, 323.15 and 333.15 K at 30, 40 and 50 wt. % of total concentration were compared with data reported in the literature [4, 5]. For the case of the aqueous solutions of blended alkanolamines, the correlation proposed in reference [5] was used to estimate the densities, the differences obtained are shown in figure 1. An excellent agreement for MDEA-H<sub>2</sub>O was obtained, the AAD was  $\pm 0.0002 \text{ g cm}^{-3}$ , for the aqueous solutions of DEA-MDEA and

DEA-AMP an AAD of  $\pm 0.0008 \text{ g cm}^{-3}$  and  $\pm 0.0011 \text{ g cm}^{-3}$  was obtained, respectively. Additionally, it was observed that the differences between our data and those reported in the literature increased as a function of temperature. The accuracy of the density data reported in this work has been estimated to be  $\pm 0.0002 \text{ g cm}^{-3}$ .

We think that the differences obtained for the pure components are due mainly to reagents purity while those obtained for DEA-MDEA and DEA-AMP are due to the correlation procedure, the data reported in reference [5] does not cover the region studied in this work.

Figure 2 shows the density data at 313.15 K and 40 wt. % for the aqueous blended solvents studied in this work, the order in the magnitude obtained was the following one: DEA + MDEA + water > DEA + NMP + water > DEA + 2PE + water > DEA + AMP + water > MDEA + AMP + water > NMP + AMP + water, this order is consistent with the pure solvent density DEA > MDEA > NMP > 2PE > AMP. The functionality observed for the density vs concentration of each of the aqueous blended solvents was linear in the range of temperature studied. From the experimental density data, molar excess volumes ( $V^E$ ) were derived, the procedure has been described widely [5]. Figure 3 shows the values obtained, all excess volumes are negatives which is common for this type of (water + polar organic) mixtures. The  $V^E$  values become less negative with increasing temperature.

#### 4. CORRELATION OF THE EXPERIMENTAL DATA:

The excess volume for a multicomponent mixture can be calculated from the molar volume of the mixture and those corresponding to the pure components, according to the following equation:

$$V^E = V_m - \sum x_i V_i^0 \dots\dots\dots(1)$$

For a ternary system, equation (1) takes the following form:

$$V^E = V_m - (x_1 V_1^0 + x_2 V_2^0 + x_3 V_3^0) \dots\dots\dots(2)$$

Analogously to what is currently used for binary systems, the excess volume for a ternary system can be considered as the result of the contributions to this value from the three pairs of components present in the ternary:

$$V_{123}^E = V_{12}^E + V_{13}^E + V_{23}^E \dots\dots\dots(3)$$

For a binary system, the polynomial Redlich-Kister equation used to represent the excess volume has the following form:

$$V_{12}^E = x_1 x_2 \sum_{i=0}^n A_i (x_1 - x_2)^i \dots\dots\dots(4)$$

Where  $A_i$  corresponds to adjustable parameters,  $x$  is the mole fraction.

Substituting equation (4) in (3), for each of the pair of components from the ternary system, the polynomial Redlich-Kister equation for a ternary system is obtained:



The same is applied to the adjustable parameters  $B_i$  and  $C_i$  in equation (5).

With the scheme above mentioned, the adjustable parameters needed to represent the excess volume, as a function of both concentration and temperature, of a ternary system are 18. The corresponding adjustable parameter values for the different ternary systems studied here were obtained using the least squares technique together with the Gauss-Newton method to fulfill the following objective function:

$$FO = \min \sum_{i=1}^N (V_{i \text{exp}}^E - V_{i \text{ical}}^E)^2 \dots \dots \dots (7)$$

The quality of the fitting procedure was established using the standard deviation, which in turn was evaluated for each ternary system, according to the following relation:

$$\sigma_{VE} = \sqrt{\frac{\sum_{i=1}^N (V_{i \text{exp}}^E - V_{i \text{ical}}^E)^2}{N - m}}$$

with  $N$ , the number of experimental points, and  $m$ , the number of adjustable parameters.

The parameters corresponding to each mixture studied along with the standard deviation of the fitting are given in table 4. It can be observed that the Redlich-Kister equation reproduces the experimental behavior suitably, an average total deviation of  $\pm 0.007 \text{ cm}^3 \text{ g mol}^{-1}$  was obtained.

## 5. CONCLUSIONS

Density data of aqueous blended solvents have been measured for 7 mixtures, the systems studied have industrial interest since they could be used for the sweetening of gas streams. The experimental information was correlated satisfactorily by the Redlich-Kister equation, the correlation procedure included the functionality with temperature which represents a contribution to works reported in Literature. The behavior observed in density and excess volume is the one that traditionally presents aqueous organic systems.

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Table 1. Review of the literature that reports density data for some of the systems studied in this work.

System	T (K)	No. of data points	Total wt. %	Ref
DEA	293–361	5		[7]
	297–433	8		[8]
	298–333	8		[3]
	298–353	7		[9]
MDEA	288–333	10		[10]
	293–361	5		[7]
	303–353	8		[11]
	296–471	8		[8]
	298–353	7		[4]
	298–343	5		[12]
NMP	283–333	11		[3]
2PE	304–357	5		[13]
AMP	305–364	6		[14]
	303–353	6		[15]
DEA(1) + H <sub>2</sub> O(2)	293–373	15	10–30	[16]
	303–353	12	20–30	[5]
	298–353	105	5.0–99.0	[9]
MDEA(1) + H <sub>2</sub> O(2)	288–333	43	10–50	[10]
	303–353	8	30	[11]
	303–353	6	20	[15]
	333–373	15	10–50	[16]
	298–353	112	5–99.2	[4]
	298–357	25	10–75	[13]
2PE(1) + H <sub>2</sub> O(2)	298–357	25	10–75	[13]
	293–364	35	9.0–88.0	[14]
AMP(1) + H <sub>2</sub> O(2)	293–364	35	9.0–88.0	[14]
	303–353	12	20–30	[15]
DEA(1) + MDEA(2) + H <sub>2</sub> O(3)	298–353	56	25.0–32.2	[17]
	293–373	20	50	[16]
	303–353	42	20–30	[5]
DEA(1) + AMP(2) + H <sub>2</sub> O(3)	303–353	42	20–30	[5]

Table 2. Summary of the systems studied in this work. Temperature range 313.15-333.15 K

System	No. of data points	Total wt. %
DEA	3	
MDEA	3	
NMP	3	
2PE	3	
AMP	3	
DEA-H <sub>2</sub> O	10	30-60
MDEA-H <sub>2</sub> O	26	10-100
NMP-H <sub>2</sub> O	11	30-60
2PE-H <sub>2</sub> O	2	30-40
AMP-H <sub>2</sub> O	10	30-60
DEA-MDEA-H <sub>2</sub> O	63	30-50
DEA-AMP-H <sub>2</sub> O	63	30-50
DEA-2PE-H <sub>2</sub> O	12	30-40
DEA-NMP-H <sub>2</sub> O	63	30-60
MDEA-AMP-H <sub>2</sub> O	63	30-50
MDEA-NMP-H <sub>2</sub> O	63	30-60
NMP-AMP-H <sub>2</sub> O	63	30-60

Table 3. Density for pure components

System	T (K)	$\rho$ (g/cm <sup>3</sup> )	
		This work	Literature
DEA	313.15	1.08469	1.0838 <sup>[3]</sup> , 1.08456 <sup>[8]</sup> , 1.08401 <sup>[9]</sup>
	323.15	1.07744	1.0771 <sup>[3]</sup> , 1.07813 <sup>[8]</sup> , 1.07732 <sup>[9]</sup>
	333.15	1.07029	1.0700 <sup>[3]</sup> , 1.07156 <sup>[8]</sup> , 1.07074 <sup>[9]</sup>
MDEA	313.15	1.02501	1.02445 <sup>[4]</sup> , 1.02483 <sup>[7]</sup> , 1.02470 <sup>[8]</sup> , 1.0267 <sup>[10]</sup> , 1.0249 <sup>[11]</sup> , 1.02519 <sup>[12]</sup>
	323.15	1.01737	1.01666 <sup>[4]</sup> , 1.01723 <sup>[7]</sup> , 1.01733 <sup>[8]</sup> , 1.0194 <sup>[10]</sup> , 1.0174 <sup>[11]</sup> , 1.01699 <sup>[12]</sup>
	333.15	1.00962	1.00900 <sup>[4]</sup> , 1.00956 <sup>[7]</sup> , 1.00987 <sup>[8]</sup> , 1.0123 <sup>[10]</sup> , 1.0098 <sup>[11]</sup> , 1.00960 <sup>[12]</sup>
NMP	313.15	1.01568	1.0120 <sup>[3]</sup>
	323.15	1.00537	1.0030 <sup>[3]</sup>
	333.15	0.99739	0.9934 <sup>[3]</sup>
2PE	313.15	0.98334	0.98487 <sup>[13]</sup>
	323.15	0.97169	0.97719 <sup>[13]</sup>
	333.15	0.96865	0.96952 <sup>[13]</sup>
AMP	313.15	0.91715	0.92110 <sup>[14]</sup> , 0.9179 <sup>[15]</sup>
	323.15	0.90923	0.91336 <sup>[14]</sup> , 0.9096 <sup>[15]</sup>
	333.15	0.90054	0.90548 <sup>[14]</sup> , 0.9011 <sup>[15]</sup>

Table 4. Ternary parameters for the Redlich-Kister equation used to calculate excess volumes for the aqueous blended solvents as a function of concentration and temperature.

Param.		DEA+MDEA	DEA+NMP	DEA+2PE	DEA+AMP	MDEA+NMP	MDEA+AMP	NMP+AMP
A <sub>0</sub>	A	-18.25474	-97.37448	-22.16388	4.801589	-106.0603	20.51124	-117.2694
	B	0.04507487	0.2902504		-0.0324989	0.3292501	-0.06642775	0.3537799
A <sub>1</sub>	A	-44.5191	136.0043	-49.88748	-488.5796	33.67065	-198.9703	-166.2908
	B	0.1789795	-0.4033312		1.535174	-0.0897512	0.6143747	0.5093373
A <sub>2</sub>	A	-7287.514	-2625.763	24.686	-3444.605	1681.678	-450.0681	-1462.653
	B	22.81695	8.005595		10.68578	-5.050315	1.705122	4.390609
B <sub>0</sub>	A	-13.9848	121.3454	-49.50577	-123.1192	115.4604	-366.035	13.24808
	B	0.07150354	-0.3769411		0.4224277	-0.3615006	1.177524	-0.02072763
B <sub>1</sub>	A	-51.35764	350.3402	-107.432	-333.8324	348.8847	-894.965	53.88767
	B	0.2596861	-1.064002		1.168453	-1.045632	2.930377	-0.06313342
B <sub>2</sub>	A	-48.47909	246.5709	-61.67413	-230.6797	239.9216	-561.8915	21.69748
	B	0.2174296	-0.7502017		0.8038396	-0.7240502	1.839228	0.01103087
C <sub>0</sub>	A	-477.4857	-140.3983	0.812425	-45.48709	-22.69931	0.9177868	-73.78735
	B	1.480019	0.4254312		0.1398934	0.06129868	-35.43701	0.1988199
C <sub>1</sub>	A	-1179.841	-317.3203	9.017947	-84.92816	15.83984	28.80812	-126.8768
	B	3.704367	1.005141		0.3036014	-0.02697802	-0.04625028	0.3524963
C <sub>2</sub>	A	-743.3084	-197.062	1.832706	-53.24203	35.55048	13.80651	-52.86822
	B	2.332726	0.6331313		0.1862061	-0.08866647	-0.01869522	0.1281156
$\sigma_{VE}$		0.0070	0.0083	0.0026	0.0087	0.0061	0.0083	0.0102

cm<sup>3</sup>mol<sup>-1</sup>

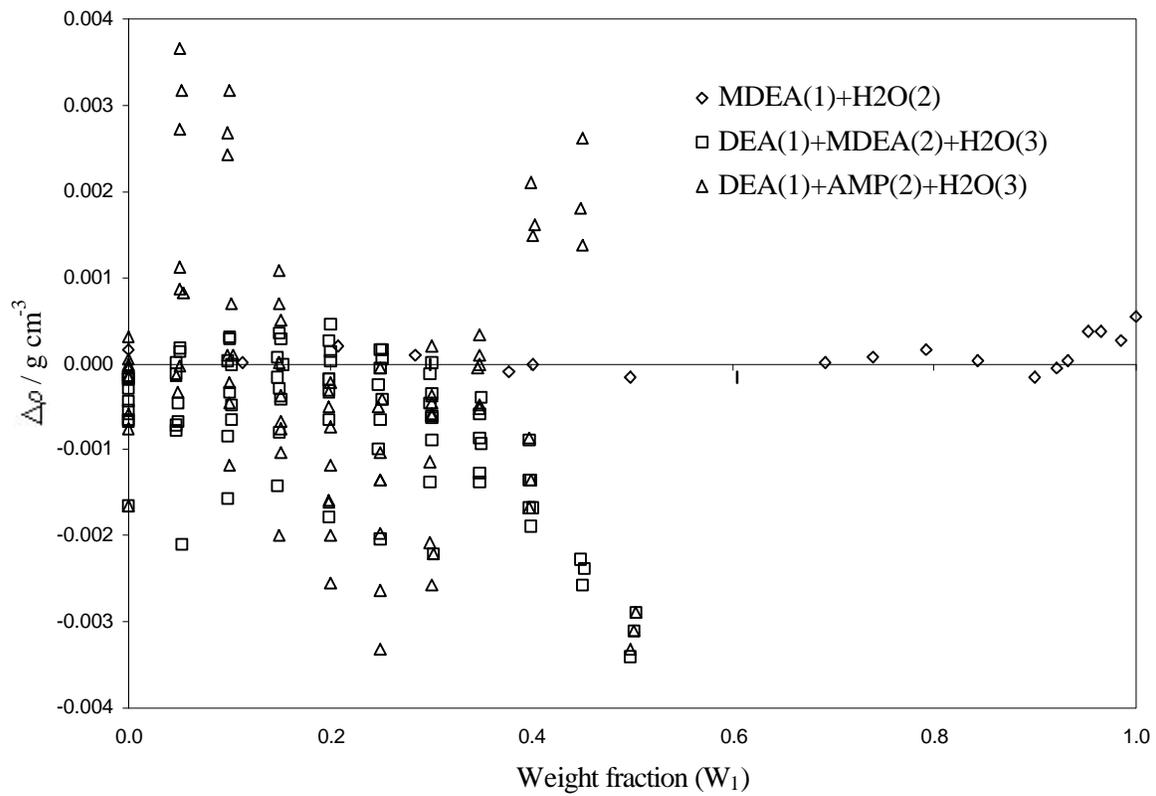


Fig. 1. Comparison between experimental and literature density data.  
 $\diamond$  Reference [4],  $\square$  Reference [16],  $\triangle$  Reference [5]

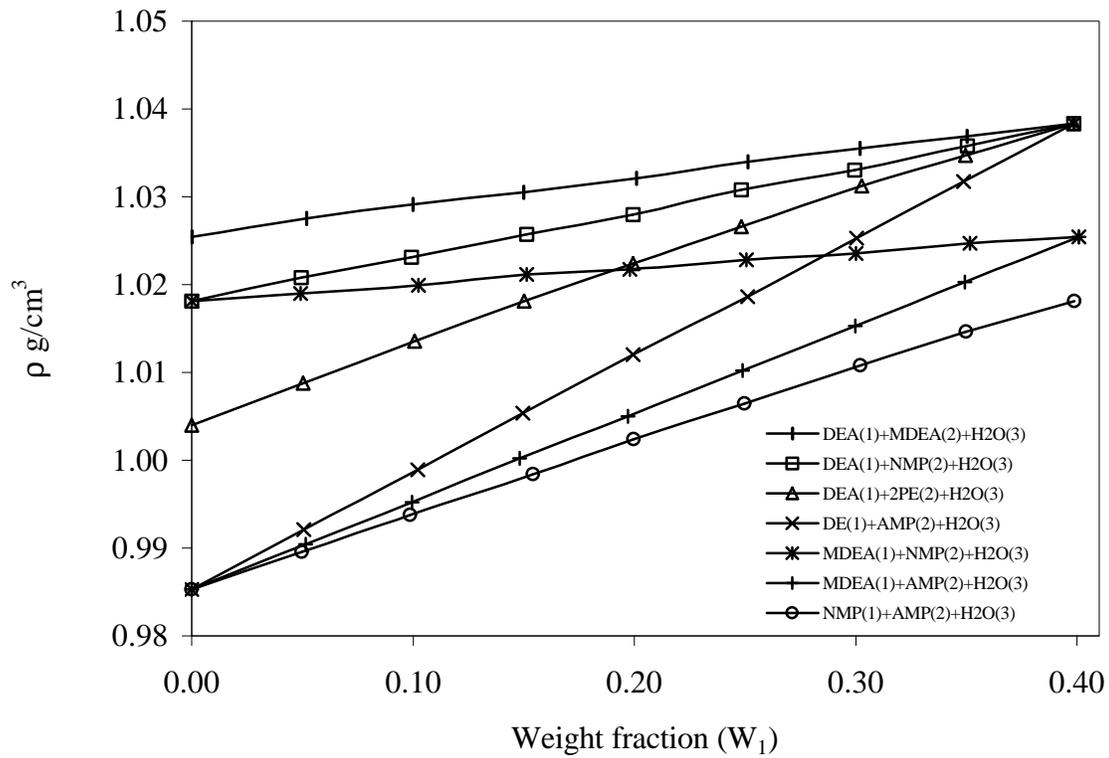


Fig. 2 Experimental density data for the aqueous blended solvents at 40 wt. % and 313.15 K.

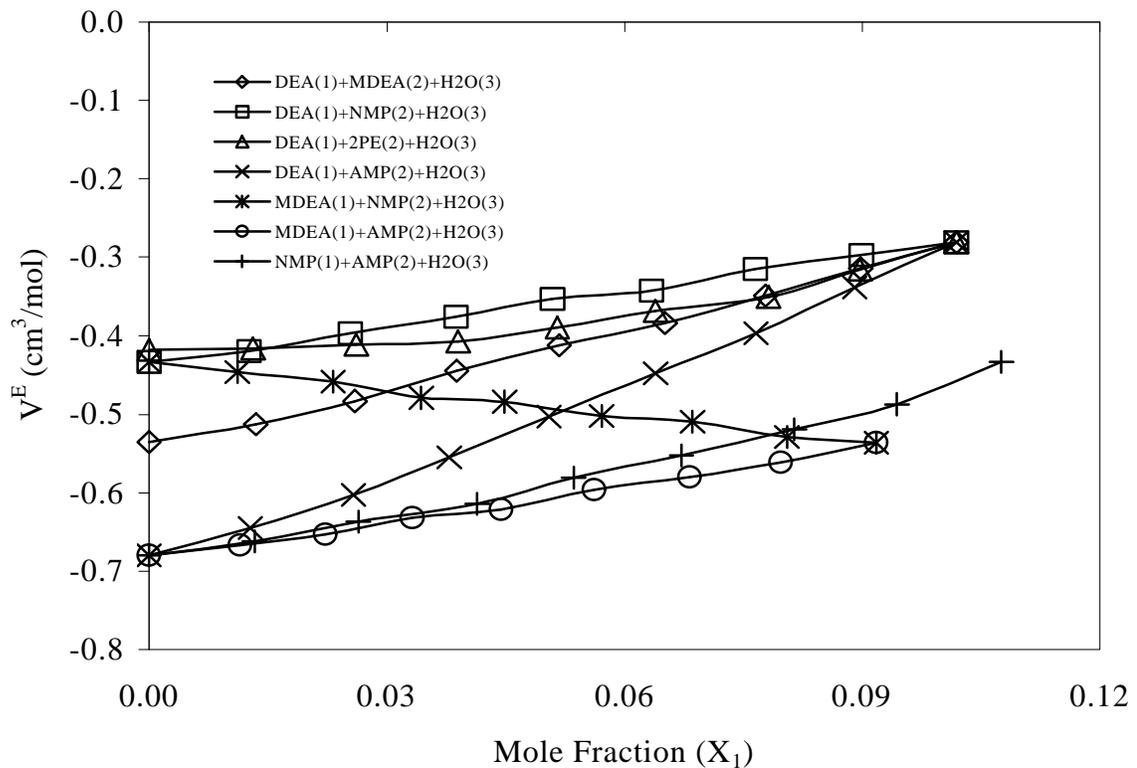


Fig. 3 Molar excess volume for the aqueous blended solvents at 40 wt. % and 313.15 K.