

# Densities of Water + Diethanolamine + Methanol and Water + *N*-Methyldiethanolamine + Methanol at Temperatures Ranging from (283.15 to 353.15) K

Fatiha Amararene,<sup>†</sup> Pierre Balz,<sup>‡</sup> Chakib Bouallou,<sup>†</sup> Renaud Cadours,<sup>‡</sup> Fabrice Lecomte,<sup>‡</sup> Pascal Mougín,<sup>‡</sup> and Dominique Richon<sup>\*,†</sup>

Ecole Nationale Supérieure des Mines de Paris, CENERG/TEP, 35 Rue Saint Honoré, 77305 Fontainebleau, France, and Institut Français du Pétrole, 1-4 avenue de Bois Préau, 92852 Rueil Malmaison Cedex, France

Two vibrating tube densimeters have been used to measure the densities of two mixtures—water + diethanolamine + methanol and water + *N*-methyldiethanolamine + methanol—in the temperature range (283 to 353) K. The alkanolamines and methanol contents are respectively (between 20 and 50 and between 20 and 60) mass %. The experimental results have been correlated using the Redlich–Kister equation for the excess volume. A set of parameters for the Redlich–Kister equation has been determined using the densities of pure compounds and of binary systems available in the literature. The methodology has been extended to density calculations dealing with hybrid solvents.

## Introduction

Aqueous alkanolamine solutions are of great interest as chemical solvents used in natural gas sweetening processes. A wide variety of alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), or methyldiethanolamine (MDEA) have been used industrially for a number of years.<sup>1</sup> MDEA and DEA are widely used in gas treatment because of their chemical properties. MDEA is generally used for selective removal of H<sub>2</sub>S in the presence of CO<sub>2</sub>, while DEA is a common solvent for total deacidification. These aqueous alkanolamine solutions have however generally quite low efficiencies when used for the removal of other sulfur species, especially mercaptans.

Moreover, when the acid gas impurities represent an appreciable fraction of the total gas stream, the cost for removing them by heat regenerable solvent absorption may be out of proportion to the value of the treated gas. This consideration has provided the major impetus for the development of processes employing nonreactive organic solvents as a treating agent. These materials dissolve physically the acid gases and are partially regenerated by merely reducing the pressure. Moreover, minor gas impurities such as carbonyl sulfide and mercaptans are quite soluble in most organic solvents and can be removed to a large extent together with the acid gases by a physical solvent.<sup>2</sup>

In contrast to the solvents mentioned previously, mixtures of chemical and physical solvents, often referred to as “mixed” or “hybrid” solvents, have been developed.<sup>3–6</sup> The absorption process resembles a conventional alkanolamine treating unit, but the presence of the physical solvent enhances the solution capacity, especially when the gas stream to be treated is at high pressure with large quantities of acid compounds and/or minor gas impurities such as carbonyl sulfide and mercaptans present.

As the gas reserves that natural gas field exploration and production have now to deal with are increasingly sour, Rojey et al.<sup>7</sup> have proposed a new sour gas treatment technology integrating dehydration, natural gas liquids (NGL) extraction, and acid gas removal steps with a single hybrid solvent (a mixture of methanol, water, and amine). This patented process produces sweet dry pipeline gas, sweet NGL, and dry pressurized acid gases. The process will be applicable to most sour to very sour, hydrocarbon-rich natural or associated gases.

This process is composed of two parts: a dew point section (used for dehydration and NGL extraction) and a sweetening section (used for acid gas removal). The solvent used in the sweetening section is a mixture of methanol, water, and an alkanolamine such as diethanolamine (DEA), which combines some of the advantages of physical solvent processes (high acid gas loadings, important affinity for COS and mercaptans) with those of chemical solvent processes (stringent specifications on H<sub>2</sub>S and CO<sub>2</sub> in the treated gas easily achieved).

The physicochemical data of solvents required for the design of acid gas treatment equipment are generally solubility data, kinetic data, and additional data such as density, viscosity, and so forth. In the context of the development of this new process, particular attention was accorded here to the solvent density. In this work, densities of two different solvents, water + DEA + methanol and water + MDEA + methanol, were measured with two vibrating tube densimeters in the temperature range (283 to 353) K, for various compositions ranging from (20 to 50) wt % alkanolamine and from (20 to 60) mass % methanol. A simplified form of the Redlich–Kister equation was applied to represent excess molar volumes.

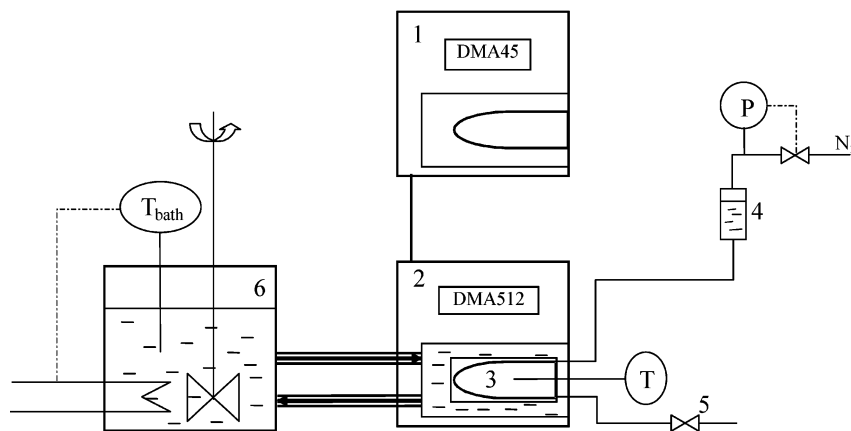
## Experimental Section

**Apparatus and Procedure.** Numerous experimental data for alkanolamine aqueous mixtures densities have been reported in the literature.<sup>8–14</sup> Most of these previous works have used atmospheric apparatus, pycnometers, or vibrating tube densimeters.

<sup>†</sup> Ecole Nationale Supérieure des Mines de Paris, CENERG/TEP.

<sup>‡</sup> Institut Français du Pétrole.

\* Corresponding author.



**Figure 1.** Experimental apparatus: 1, DMA45 densimeter; 2, DMA512 remote cell; 3, measuring cell; 4, solvent reserve; 5, stop valve; 6, thermostated bath.

In this work, two apparatuses in two different laboratories have been used to measure liquid densities. Both are vibrating tube densimeter type. The first one allows density measurement under pressure by using a special remote cell; the second one was a standard atmospheric apparatus similar to those described in the open literature. The consistency of the different experimental results was checked against any systematic error.

The first apparatus, manufactured by Anton Paar, is a vibrating tube densimeter type DMA512, which is a special remote cell for density measurement under pressure. The sample tube, made of stainless steel, was housed in a thermostated brass jacket. The measuring cell temperature was regulated to within 0.05 K with a HAAKE K15/DC30 liquid bath. The cell temperature was measured with a platinum probe calibrated within 0.01 K against a 25- $\Omega$  platinum probe type 1/622C manufactured by Rosemount. This remote cell was connected to an Anton Paar DMA45 densimeter used as a processing unit. Densities  $\rho$  were calculated from the period of vibration  $\tau$ :

$$\rho = A + B\tau^2 \quad (1)$$

The constants  $A$  and  $B$  were determined as a function of temperature by calibrating the apparatus with reference fluids of known densities, taking into account the conclusions of Bouchot and Richon.<sup>15</sup> The DMA45 + DMA512 set was calibrated within 0.001 g·cm<sup>-3</sup> with pure water and pure alcohol with the same process in the temperature range (293 to 353) K.

The following procedure was applied to apparatus calibration and density measurements. The liquid sample from the solvent supply was introduced into the vibrating tube of the DMA512 densimeter (Figure 1). All the tubing was filled with the liquid. The stop valve was closed. The liquid sample was then pressurized to 0.7 MPa with nitrogen. This procedure was used to prevent the appearance of gas bubbles in the measuring cell, which occurs at high temperatures. The gas–solvent interface was located in the solvent reserve, and the tubing length avoids the introduction of N<sub>2</sub> into the measuring cell by diffusion through the solvent during the time of the experiment.

For each sample, the vibration period was then measured at temperatures ranging from (303 to 353) K by successive temperature increments. This operation was performed with increasing and decreasing temperatures to prove that no hysteresis effects need to be considered with temperature changes. Densities are then calculated, and each

**Table 1.** Experimental Conditions for Density Measurements

solvent	$T/K$	$w_2$	$w_3$	experimental method
Water (1) + DEA (2) + Methanol (3)				
solvent 1	293–353	0.200	0.200	DMA45 + DMA512
solvent 2	293–353	0.200	0.400	DMA45 + DMA512
solvent 3	293–353	0.300	0.200	DMA45 + DMA512
solvent 4	293–353	0.300	0.300	DMA45 + DMA512
solvent 5	293–353	0.300	0.500	DMA45 + DMA512
solvent 6	293–353	0.300	0.600	DMA45 + DMA512
solvent 7	293–353	0.400	0.400	DMA45 + DMA512
solvent 8	278–353	0.301	0.199	DMA5000
solvent 9	278–353	0.400	0.200	DMA5000
solvent 10	278–353	0.401	0.397	DMA5000
Water (1) + MDEA (2) + Methanol (3)				
solvent 11	293–353	0.200	0.200	DMA45 + DMA512
solvent 12	293–353	0.200	0.400	DMA45 + DMA512
solvent 13	293–353	0.300	0.300	DMA45 + DMA512
solvent 14	293–353	0.300	0.500	DMA45 + DMA512
solvent 15	293–353	0.400	0.200	DMA45 + DMA512
solvent 16	293–353	0.400	0.400	DMA45 + DMA512
solvent 17	283–353	0.200	0.401	DMA5000
solvent 18	283–353	0.302	0.396	DMA5000
solvent 19	283–353	0.303	0.495	DMA5000
solvent 20	283–353	0.398	0.301	DMA5000
solvent 21	283–353	0.400	0.398	DMA5000
solvent 22	283–353	0.399	0.495	DMA5000
solvent 23	283–353	0.496	0.300	DMA5000
solvent 24	283–353	0.498	0.397	DMA5000
solvent 25	283–353	0.399	0.301	DMA5000

reported value is the average of at least three measurements within an uncertainty of  $\pm 0.001$  g·cm<sup>-3</sup>.

The second apparatus used in this study is an Anton-Paar digital vibrating glass tube densimeter (model DMA5000), with a precision of  $10^{-5}$  g·cm<sup>-3</sup>. The temperature was determined with a platinum resistance thermometer with an accuracy of 0.001 K. The DMA5000 was calibrated with bidistilled and degassed water, and air. Uncertainty has been estimated to within  $\pm 0.0002$  g·cm<sup>-3</sup>.

The sample density was measured at thermal equilibrium after changing the temperature from (283 to 353) K following successive increments. This operation is performed twice for each solution. Then each reported density is the average of two measurements.

**Solutions Preparation.** Mixed solvents were prepared from water, methanol, and DEA/MDEA. Water was distilled and degassed under a vacuum. Methanol (99.8 mass % purity) from Merck was also degassed under a vacuum. DEA (99 mass % purity) was purchased from Aldrich, and MDEA (98 mass % purity) was purchased from Fluka. All chemicals were used without any further purification.

The solutions were prepared gravimetrically at ambient temperature in initially evacuated 20 cm<sup>3</sup> glass bottles (the resulting pressure is the vapor pressure of the mixed

**Table 2. Density of (Water + DEA + Methanol) Solvents**

solvent <sup>a</sup>	<i>T</i> /K	$\rho$ /g·cm <sup>-3</sup>	solvent <sup>a</sup>	<i>T</i> /K	$\rho$ /g·cm <sup>-3</sup>
1	293.15	0.990	7	293.15	0.962
	298.15	0.987		298.15	0.958
	303.15	0.985		303.15	0.954
	308.15	0.982		308.15	0.951
	313.15	0.978		313.15	0.947
	323.05	0.972		323.05	0.938
	333.05	0.965		333.05	0.929
	343.05	0.957		343.05	0.921
	352.95	0.950		352.95	0.912
	2	293.15		0.950	8
298.15		0.947	283.14	1.0064	
303.15		0.944	288.14	1.0036	
308.15		0.940	293.15	1.0007	
313.15		0.936	298.15	0.9978	
323.05		0.928	303.14	0.9947	
333.05		0.919	308.14	0.9916	
343.05		0.911	313.15	0.9884	
352.95		0.902	318.15	0.9851	
3		293.15	1.001	9	
	298.15	0.998	328.14		0.9783
	303.15	0.995	333.15		0.9748
	308.15	0.992	338.14		0.9712
	313.15	0.988	343.15		0.9674
	323.05	0.981	348.15		0.9636
	333.05	0.973	353.15		0.9597
	343.05	0.966	358.14		0.9557
	352.95	0.958	278.15		1.0162
	4	293.15	0.980		10
298.15		0.977	303.15	1.0037	
303.15		0.974	308.15	1.0004	
308.15		0.971	323.15	0.9901	
313.15		0.966	328.15	0.9865	
323.05		0.958	333.15	0.9829	
333.05		0.950	338.15	0.9792	
343.05		0.942	343.15	0.9754	
352.95		0.934	348.15	0.9715	
5		293.15	0.931	11	
	298.15	0.928	278.15		0.9736
	303.15	0.924	283.15		0.9700
	308.15	0.920	288.18		0.9664
	313.15	0.916	293.15		0.9628
	323.05	0.907	298.15		0.9591
	333.05	0.898	303.15		0.9554
	343.05	0.892	308.15		0.9517
	352.95	0.883	313.15		0.9479
	6	293.15	0.903		12
298.15		0.900	338.15	0.9281	
303.15		0.895	343.15	0.9239	
308.15		0.892	353.15	0.9155	
313.15		0.887			
323.05		0.879			
333.05		0.869			
343.05		0.861			
352.95		0.851			

<sup>a</sup> See Table 1 for solvent composition.

solvent) using a Mettler AT 200 balance with an accuracy of 10<sup>-4</sup> g.

The procedure was the following: (1) the bottles were first evacuated with a vacuum pump; (2) the empty bottles were weighed; (3) degassed DEA or MDEA was introduced in the bottles by means of a syringe; (4) the bottles loaded with DEA or MDEA were weighed; (5) degassed water and degassed methanol were added successively, and the bottles were weighed after each addition. Finally, the composition of the solution was determined from the different masses. The solution was then transferred into the solvent reserve for DMA45 + DMA512 equipment (measurement under pressure) or directly introduced into the DMA5000 densimeter cell (measurement under atmospheric pressure). The compositions for each solvent, and the corresponding density measurement method, are reported in Table 1.

**Results.** The densities of the different solvents, water + DEA + methanol and water + MDEA + methanol, are reported in Tables 2 and 3, respectively, at several compositions and for temperatures ranging from (283 to 353) K.

We have compared for the similar solvent compositions the densities obtained with both sets of equipment (DMA45

**Table 3. Density of (Water + MDEA + Methanol) Solvents**

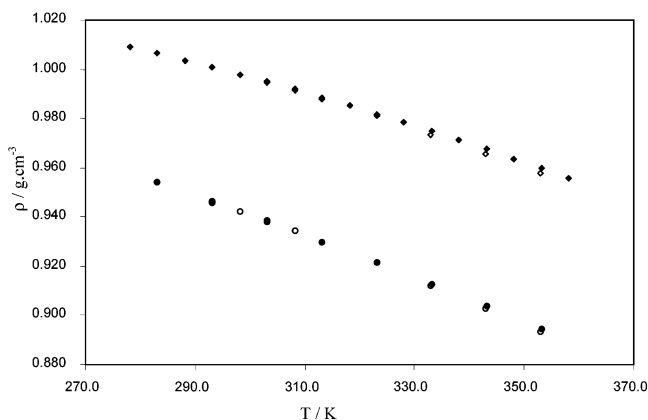
solvent <sup>a</sup>	<i>T</i> /K	$\rho$ /g·cm <sup>-3</sup>	solvent <sup>a</sup>	<i>T</i> /K	$\rho$ /g·cm <sup>-3</sup>		
11	293.15	0.985	18	283.15	0.9512		
	298.15	0.982		293.15	0.9437		
	303.15	0.978		303.15	0.9363		
	313.15	0.972		313.15	0.9286		
	323.05	0.965		323.15	0.9206		
	333.05	0.958		333.15	0.9122		
	343.05	0.950		343.15	0.9036		
	352.95	0.941		353.15	0.8946		
	12	293.15		0.945	19	283.15	0.9260
		298.15		0.941		293.15	0.9177
303.15		0.938	303.15	0.9094			
313.15		0.929	313.15	0.9009			
323.05		0.921	323.15	0.8923			
333.05		0.913	333.15	0.8834			
343.05		0.904	343.15	0.8744			
352.95		0.894	353.15	0.8651			
13		293.15	0.971	20		283.15	0.9799
		298.15	0.967			293.15	0.9724
	303.15	0.964	303.15		0.9645		
	308.15	0.960	313.15		0.9564		
	313.15	0.956	323.15		0.9481		
	323.05	0.948	333.15		0.9396		
	333.05	0.939	343.15		0.9309		
	343.05	0.930	353.15		0.9218		
	352.95	0.922	21		283.15	0.9541	
	14	293.15			0.920	293.15	0.9462
298.15		0.916		303.15	0.9381		
303.15		0.912		313.15	0.9298		
313.15		0.904		323.15	0.9214		
323.05		0.895		333.15	0.9127		
333.05		0.886		343.15	0.9038		
343.05		0.877		353.15	0.8946		
352.95		0.867		22	283.15	0.9291	
15		293.15			0.997	293.15	0.9211
		298.15	0.994		303.15	0.9129	
	303.15	0.990	313.15		0.9045		
	308.15	0.986	323.15		0.8959		
	313.15	0.982	333.15		0.8871		
	323.05	0.974	343.15		0.8780		
	333.05	0.965	353.15		0.8687		
	343.05	0.956	23		283.15	0.9803	
	352.95	0.948			293.15	0.9725	
	16	293.15		0.946	303.15	0.9647	
298.15		0.942		313.15	0.9567		
303.15		0.939		323.15	0.9486		
308.15		0.935		333.15	0.9401		
313.15		0.930		343.15	0.9315		
323.05		0.922		353.15	0.9225		
333.05		0.912		24	283.15	0.9547	
343.05		0.903			293.15	0.9470	
352.95		0.894	303.15		0.9392		
17		283.15	0.9509		313.15	0.9312	
	293.15	0.9430	323.15		0.9229		
	303.15	0.9348	333.15		0.9144		
	313.15	0.9265	343.15		0.9055		
	323.15	0.9180	353.15		0.8964		
	333.15	0.9093	25		283.15	0.9799	
	343.15	0.9005			293.15	0.9723	
	353.15	0.8914		303.15	0.9645		
				313.15	0.9564		
				323.15	0.9481		
		333.15		0.9396			
		343.15		0.9308			
		353.15		0.9218			

<sup>a</sup> See Table 1 for solvent composition.

+ DMA512 and DMA5000) used in this study. As shown in Figure 2 the densities obtained through the two sets of equipment are in good agreement. Some differences appear at the higher temperatures. However, they generally remain within the uncertainties of the experimental methods. Moreover, they can be explained by the slight differences in the solvent compositions and by the different operating pressures, 0.7 MPa for the DMA45 + DMA512 and atmospheric pressure for the DMA5000.

## Discussion

The density of water + alkanolamine + methanol systems was represented with a similar approach to those previously used by Rinker et al.<sup>13</sup> and Hsu and Li<sup>16</sup> for



**Figure 2.** Comparison of the two experimental techniques: ◆, (50–30–20) mass % H<sub>2</sub>O + DEA + MeOH; ◇, (50–30–20) mass % H<sub>2</sub>O + DEA + MeOH; ●, (20–40–40) mass % H<sub>2</sub>O + DEA + MeOH; ○, (20–40–40) mass % H<sub>2</sub>O + DEA + MeOH.

**Table 4.** Density of Pure DEA and Pure MDEA

ref	<i>T</i> /K	no. of points	deviation <sup>a</sup> (%)
DEA			
20	293.15–353.15	4	0.11
21	298.15–333.15	8	0.03
22	298.15–393.15	6	0.09
23	293.15–361.15	5	0.09
13	298.15–363.15	5	0.24
18*	283.15–363.15	18	0.04
14*	183.15–373.15	10	0.03
8*	298.15–353.15	7	0.03
MDEA			
22	296.15–398.15	5	0.12
24	303.15–353.15	8	0.08
23	293.15–361.15	5	0.06
13	298.15–366.15	6	0.31
18*	283.15–363.15	17	0.06
14*	293.15–393.15	9	0.27
8*	298.15–353.15	7	0.05

<sup>a</sup> Deviation  $U = (100/n)\sum((U_{\text{exp}} - U_{\text{cal}})/U_{\text{exp}})$ .

water + alkanolamines binary and ternary systems:

$$\rho = \frac{M_m}{V_m} = \frac{\sum x_i M_i}{V_m} \quad (2)$$

where  $M_m$  was the molar mass of the mixture,  $M_i$  was the molar mass of the pure compound  $i$ , and  $x_i$  was the mole fraction of component  $i$ . The molar volume of the liquid mixture  $V_m$  was calculated from eq 3:

$$V_m = \sum x_i V_i + V^E \quad (3)$$

where  $V^E$  is the excess volume and  $V_i$  is the molar volume of component  $i$ .

A Redlich–Kister type equation was applied for the excess molar volume:

$$V_{12}^E/\text{cm}^3 \cdot \text{mol}^{-1} = x_1 x_2 (A_0 + A_1 T(\text{K}) + A_2 x_1) \quad (4)$$

$T$  is the temperature and  $A_0$ ,  $A_1$ , and  $A_2$  are binary parameters; cf. Table 6. The excess volume  $V^E$  of the liquid mixture for a ternary system was obtained from the excess molar volume of each binary system:

$$V^E = V_{12}^E + V_{13}^E + V_{23}^E \quad (5)$$

The method was based on the molar volumes of each pure compound, as well as on the representation of the two water + alkanolamine and water + methanol binary

**Table 5.** Density of Binary Systems

H <sub>2</sub> O–DEA				
ref	<i>T</i> /K	DEA mass %	no. of points	deviation <sup>a</sup> (%)
20	293.15–353.15	20–100	20	0.60
25	293.15–303.15	0–100	33	0.07
26	298.15	0–30	10	0.15
8*	298.15–353.15	0–100	119	0.05
12	298.15	10–40	4	0.06
16	313.15–353.15	20–30	12	0.06
13	293.15–373.15	10–100	22	0.11
14*	283.15–363.15	0–100	171	0.04
H <sub>2</sub> O–MDEA				
ref	<i>T</i> /K	MDEA mass %	no. of points	deviation <sup>a</sup> (%)
27	288.15–308.15	10–20	12	0.78
28	288.15–333.15	0–50	53	0.05
24	303.15–353.15	30	8	0.06
9	303.15–333.15	20–30	8	0.06
8*	298.15–353.15	0–100	126	0.10
29	303.15–323.15	30–40	5	0.05
11	283.15–353.15	50	5	0.06
12	298.15	30–60	4	0.24
13	333.15–373.15	10–100	18	0.16
14*	283.15–373.15	0–100	135	0.17
H <sub>2</sub> O–Methanol				
ref	<i>T</i> /K	methanol mass %	no. of points	deviation <sup>a</sup> (%)
open lit.	273.15–353.15	0–100	>700	0.19

<sup>a</sup> Deviation  $U = (100/n)\sum((U_{\text{exp}} - U_{\text{cal}})/U_{\text{exp}})$ .

**Table 6.** Binary Parameters of the Redlich–Kister Equation

binary pairs	$A_0/\text{cm}^3 \cdot \text{mol}^{-1}$	$A_1/\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$A_2/\text{cm}^3 \cdot \text{mol}^{-1}$
DEA + H <sub>2</sub> O	−5.398 20	$6.321 9 \times 10^{-3}$	1.942 42
MDEA + H <sub>2</sub> O	−10.462 2	0.011 22	4.079 36
DEA + MeOH	2.551 49	$-1.948 42 \times 10^{-2}$	0.521 99
MDEA + MeOH	4.989 25	−0.011 38	−30.159 51
H <sub>2</sub> O–MeOH	−0.437 07	−0.010 66	−0.328 74
DEA–MDEA	−11.152 59	0.034 82	0

systems. The binary parameters for these two systems were determined from experimental data. The representation of the ternary systems was then realized by fitting the parameters alkanolamine + methanol from the experimental data obtained for the ternary systems. Therefore, the developed model will not allow representing the density of the binary systems alkanolamine + methanol.

**Representation of Molar Volumes of Pure Compounds.** The molar volumes of water and methanol were obtained from the correlations of Rinker et al.<sup>13</sup> and DIPPR.<sup>17</sup>

$$V_{\text{methanol}}/\text{cm}^3 \cdot \text{mol}^{-1} = 1000 \times \frac{0.27073^{(1+(1-[T(\text{K})]/512.5)^{0.24713})}}{2.3267} \quad (6)$$

$$V_{\text{H}_2\text{O}}/\text{cm}^3 \cdot \text{mol}^{-1} = \frac{18.02}{0.753597 + (1.877465 \times 10^{-3})T(\text{K}) - (3.563982 \times 10^{-6})T^2(\text{K}^2)} \quad (7)$$

For DEA and MDEA, we have selected the literature data which appear to be the most consistent with the temperature and composition ranges studied and according to the consistency of these data between each other.<sup>8,14,18</sup> These data are identified with an asterisk in Table 4. They have been obtained by means of a vibrating glass tube

Table 7. Density of Ternary Systems

H <sub>2</sub> O–DEA–Methanol					
apparatus	<i>T</i> /K	DEA mass %	methanol mass %	no. of points	deviation <sup>a</sup> (%)
DMA45 + DMA512	293.15–353.15	20–40	0–60	64	0.09
DMA5000	278.15–353.15	30–40	0–40	54	0.04
H <sub>2</sub> O–MDEA–Methanol					
apparatus	<i>T</i> /K	MDEA mass %	methanol mass %	no. of points	deviation <sup>a</sup> (%)
DMA45 + DMA512	293.15–353.15	20–40	20–50	51	0.13
DMA5000	283.15–353.15	20–50	30–50	64	0.20

<sup>a</sup> Deviation  $U = (100/n)\Sigma((U_{\text{exp}} - U_{\text{cal}})/U_{\text{exp}})$ .

densimeter, and they present experimental uncertainties lower than  $0.001 \text{ g}\cdot\text{cm}^{-3}$  and a good consistency between the various sources. The following correlations were obtained from these data:

$$V_{\text{DEA}}/\text{cm}^3\cdot\text{mol}^{-1} = \frac{105.16}{1.2968 - (6.8008 \times 10^{-4})T(\text{K})} \quad (8)$$

$$V_{\text{MDEA}}/\text{cm}^3\cdot\text{mol}^{-1} = \frac{119.16}{1.27462 - (7.9703 \times 10^{-4})T(\text{K})} \quad (9)$$

Table 4 shows the deviation between these correlations and the literature data and contains the regressed data sources.

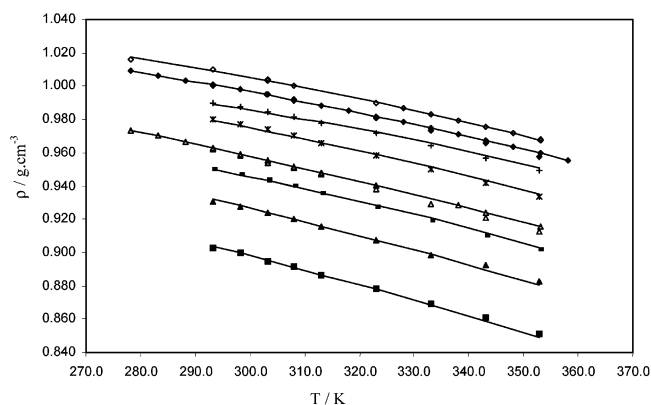
**Representation of Water + Alkanolamine and Water + Methanol Binary Systems.** The binary parameters for DEA + water and MDEA + water, were determined from literature data. As for the pure components, consistent data (displayed with an asterisk in Table 5) were selected in the open literature for the determination of the correlation parameters. The representation of the consistent data was achieved within an average absolute percentage deviation of 0.04% and 0.14%, respectively, for the water + DEA and water + MDEA systems.

More than 800 experimental data points are available in the open literature for the water + methanol system, over a large range of temperatures (163 to 353 K) and compositions. All of them are collected in the Dortmund Data Bank.<sup>19</sup> We have retained the more consistent data for the identification of the water + methanol binary parameters, in the temperature range (273.15 to 353.15) K (Table 5). All the determined binary parameters are reported in Table 6.

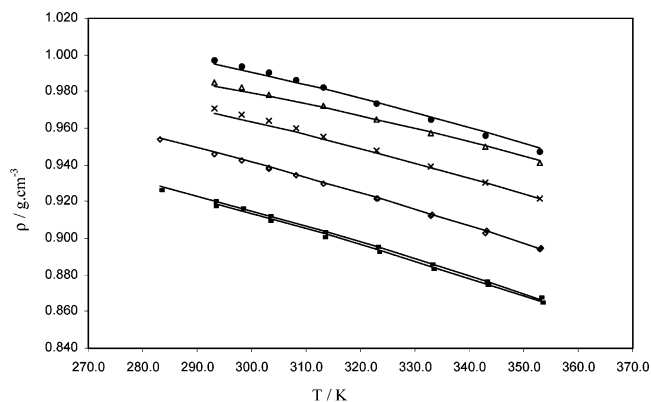
**Representation of Water + Alkanolamine + Methanol Ternary Systems.** As mentioned above, the representation of the ternary system was obtained by fitting the alkanolamine + methanol binary parameters from density data of ternary systems. This approach ensured a good representation of the water + alkanolamine + methanol system, within (0.07 and 0.16)% deviation for water + DEA + methanol and water + MDEA + methanol ternary systems, respectively, as shown in Table 7 and Figures 3 and 4.

## Conclusion

The densities of the solvent systems (water + DEA + methanol) and (water + MDEA + methanol) have been measured using two apparatuses, the first one for density measurement under pressure and the second one for density measurement under atmospheric pressure. Measurements were performed for temperatures ranging from (283 to 353) K and for several compositions. We obtained good reproducibility, and at temperatures below 353 K, we have observed an excellent agreement between the two



**Figure 3.** Density of the water + DEA + methanol system:  $\square$ , (10–30–60) mass % H<sub>2</sub>O + DEA + MeOH; small box, (40–20–40) mass % H<sub>2</sub>O + DEA + MeOH;  $\blacktriangle$ , (20–30–50) mass % H<sub>2</sub>O + DEA + MeOH; \*, (40–30–30) mass % H<sub>2</sub>O + DEA + MeOH;  $\Delta$ , (20–40–40) mass % H<sub>2</sub>O + DEA + MeOH;  $\blacklozenge$ , (50–30–20) mass % H<sub>2</sub>O + DEA + MeOH;  $\diamond$ , (40–20–20) mass % H<sub>2</sub>O + DEA + MeOH; +, (60–20–20) mass % H<sub>2</sub>O + DEA + MeOH; –, calculated values.



**Figure 4.** Density of the water + DEA + methanol system:  $\blacksquare$ , (20–30–50) mass % H<sub>2</sub>O + DEA + MeOH;  $\diamond$ , (20–40–40) mass % H<sub>2</sub>O + DEA + MeOH;  $\times$ , (40–30–30) mass % H<sub>2</sub>O + DEA + MeOH;  $\bullet$ , (40–40–20) mass % H<sub>2</sub>O + DEA + MeOH;  $\Delta$ , (60–20–20) mass % H<sub>2</sub>O + DEA + MeOH; –, calculated values.

methods within their estimated uncertainties. The densities of liquid mixtures have been correlated using a Redlich–Kister equation for the excess volume. On the basis of the densities of pure compounds and of binary systems available in the literature, a set of parameters in the Redlich–Kister equation was determined. The methodology has been extended to the density calculations for the hybrid solvents. Satisfactory results were obtained for the (water + DEA + methanol) and (water + MDEA + methanol) solvents, within an overall average absolute percentage deviation of 0.12%.

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