412 *J. Chem. Eng. Data* **2005,** *50,* 412−418

Volumetric Properties of Water + Monoethanolamine + Methanol Mixtures at Atmospheric Pressure from 283.15 to 353.15 K

Christophe Coquelet,[†] Alain Valtz,[‡] and Dominique Richon*

Laboratoire de Thermodynamique des Équilibres Entre Phases, Centre d'Energétique, Ecole Nationale
Supérieure des Mines de Paris, CEP/TEP, 35 Rue Saint Honoré, 77305 Fontainebleau, France

Densities of the water + methanol binary system and of the water + monoethanolamine + methanol ternary system were measured at atmospheric pressure over the whole range of composition at temperatures from (283.15 to 353.15) K using an Anton Paar digital vibrating glass tube densimeter. The density of water + methanol binary system increases with increasing water content. The experimental excess volume data were correlated using the Redlich−Kister equation for which optimized sets of parameters are provided at each temperature. Infinite dilution partial molar volumes have been calculated for each component and tabulated. A correlation implying specific interaction parameters adjusted for ternary excess volumes along with excess volume values of the corresponding binary systems is proposed to represent the excess volume data of the ternary system.

Introduction

Aqueous alkanolamine solutions are of great interest as chemical solvents used in natural gas sweetening processes. Combining a physical solvent with a chemical solvent is judicious for this type of removal purpose. Methanol is a good candidate. The presence of a physical solvent enhances the solution capacity.[1] In designing acid gas treatment equipment, the main data required by industry are solubility data, kinetic data, densities, viscosities, and so forth. In this paper, we are dealing with the densities of the monoethanolamine (MEA) + H_2O + MeOH ternary mixture. Few publications report the densities of aqueous MEA solutions,[2−4] and none report the densitity of the MEA + H_2O + MeOH ternary system. To represent the MEA + H_2O + MeOH ternary mixture, it is necessary to have accurate modeling of the three concerned binaries. (Accurate modeling of the three concerned binaries must be performed.) Density data of MEA + MeOH mixtures are available in one of our previous papers,[5] and density data of aqueous MEA mixtures are available in the literature.[2−4]

Densities of H_2O + MeOH mixtures and of the ternary system have been measured using a vibrating tube densimeter in the temperature range of (283.15 to 353.15) K for the whole composition range and are tabulated herein.

Experimental Section

Monoethanolamine ($H_2NC_2H_4OH$, certified GC purity >99%) and methanol (CH_3OH, certified GC purity >99.93%) were obtained from Aldrich. The MEA density measured at 297.15 K is 1.01294 g·cm^{-3}, and the MeOH density measured at 298.15 K is 0.78658 g·cm^{-3} (0.7868 g·cm^{-3} from Machado and Streett[6]). The water comes from an apparatus that delivers ultrapure water (from Millipore). Water, MEA, and MeOH were carefully degassed before use, and mixtures were prepared gravimetrically under vacuum. The apparatus used for density measurements was an Anton Paar digital vibrating glass tube densimeter (model DMA5000) with a certified precision of 10^{-5} g·cm^{-3}. The following relationship holds for the period of vibration, τ, and the density, d.

$$d = a + b\tau^2 \tag{1}$$

The temperature was determined with a platinum resistance thermometer with an accuracy of 0.01 K. The DMA5000 was calibrated at 293.15 K (for the determination of the a and b constants) with bidistilled and degassed water and dry air. The sample density was measured at thermal equilibrium after changing the temperature following successive increments.

The following procedure was applied to the preparation and the loading of pure compounds and mixtures into the vibrating tube. Empty glass bottles of 20 cm^3 were closed airtight with a septum and then evacuated with the help of a vacuum pump. The empty bottle was weighed, and then the less volatile component, freshly degassed by vacuum distillation, was introduced by means of a syringe. After weighing the bottle loaded with the first component, a second component was added similarly, and then the bottle was weighed again and again after introducing a third component (in the case of a ternary mixture). The order of compound introduction was from the less volatile to the most volatile. All weighing was performed using an analytical balance with an accuracy of 0.0003 g; therefore, the average uncertainty in mole fraction is estimated to be less than 0.0003 for the binary system (($\Delta x_i/x_i \le 3(\Delta m_i/m_i)$, with m_i being the mass of the component i and $\Delta m_i = 0.0003g$ being the accuracy of the balance). Concerning the ternary system, the uncertainty in mole fraction is estimated to be less than 0.0005.

The above-described preparation and loading procedure was followed not only to obtain accurate compositions but also to avoid the formation of gas bubbles inside the vibrating tube; this happens at high temperatures when liquids are not degassed enough.

---

* Corresponding author. E-mail: dominique.richon@ensmp.fr. Tel: 331-6469-4965. Fax: 331-6469-4968.
[†] E-mail: christophe.coquelet@ensmp.fr.
[‡] E-mail: alain.valtz@ensmp.fr.

10.1021/je049691v CCC: $30.25

Table 1. Critical Temperature for Each Component and Parameters of Equation 2

component	T_C/K[a]	A/kmol·m^{-3}	B	C
MEA	678.20	1.0002[b]	0.2244[b]	0.2238[b]
MeOH	512.64	1.4791[b]	0.2176[b]	0.1971[b]
Water	647.13	5.4590[a]	0.30542[a]	0.0810[a]

[a] Values from ref 7. [b] Values from ref 5.

Binary Systems

Water + Methanol System. The correlation (eq 2) from Reid et al.[7] is used to calculate the pure-component molar densities of water and methanol.

$$d_i^*/\text{g·cm}^{-3} = \frac{A}{B^{[1 + (1 - T/T_C)^C]}} \times \frac{M_i}{1000} \tag{2}$$

M_i is the molar mass of the water or methanol component. The A, B, and C parameters are given in Table 1. MeOH parameters of eq 2 are from Valtz et al.,[5] and water parameters are from Reid et al.[7]

Densities of the binary mixture are reported in Table 2.

Excess molar volumes, plotted in Figure 1, are calculated through eq 3:

$$V^E = V - x_1V_1^* - x_2V_2^* \tag{3}$$

where V is the molar volume of the mixture water (1) + MeOH (2); see Table 2. V_1^* and V_2^* are the molar volumes of the pure components determined with eq 2 and parameters from Table 1.

By introducing the density d, eq 3 can be written as

$$V^E = \left[\frac{x_1M_1 + x_2M_2}{d}\right] - \frac{x_1M_1}{d_1^*} - \frac{x_2M_2}{d_2^*} \tag{4}$$

M_1 and M_2 are, respectively, the molar masses of water and MeOH. The Redlich−Kister[8] equation (fifth order) is applied for the excess molar volumes. (See Figure 1.)

$$V^E = x_1x_2\sum_i A_i(x_1 - x_2)^i \tag{5}$$

with $i \leq 5$.

The Redlich−Kister coefficients (A_n) have been determined at each temperature and are presented in Table 3 along with the variance, σ, corresponding to each fit.

$$\sigma = \left[\sum\frac{(V^E - V^E_{\text{calcd}})^2}{N_{\text{exp}} - 6}\right] \tag{6}$$

N_{exp} is the number of experimental data points.

Table 2. Densities (*d*) for H_2O (1) + MeOH (2) Binary Mixtures at Various Temperatures

x_1	d/g·cm^{-3}	d/g·cm^{-3}	d/g·cm^{-3}	d/g·cm^{-3}	d/g·cm^{-3}
	T = 283.15 K	T = 288.15 K	T = 293.15 K	T = 298.15 K	T = 303.15 K
0.0800	0.81374	0.80922	0.80467	0.80010	0.79552
0.1581	0.82714	0.82275	0.81833	0.81388	0.80940
0.2401	0.84201	0.83775	0.83345	0.82911	0.82474
0.3206	0.85715	0.85302	0.84884	0.84462	0.84035
0.3987	0.87239	0.86839	0.86435	0.86025	0.85610
0.4799	0.88859	0.88477	0.88088	0.87694	0.87293
0.5600	0.90516	0.90156	0.89788	0.89414	0.89032
0.6407	0.92205	0.91874	0.91533	0.91185	0.90828
0.7201	0.93863	0.93571	0.93267	0.92954	0.92631
0.8000	0.95482	0.95247	0.94998	0.94737	0.94461
0.8801	0.97045	0.96891	0.96717	0.96523	0.96312
0.9603	0.98805	0.98731	0.98629	0.98501	0.98349
	T = 308.15 K	T = 313.15 K	T = 318.15 K	T = 323.15 K	T = 328.15 K
0.0800	0.79090	0.78624	0.78154	0.77680	0.77201
0.1581	0.80488	0.80030	0.79569	0.79104	0.78632
0.2401	0.82031	0.81584	0.81130	0.80671	0.80207
0.3206	0.83603	0.83164	0.82720	0.82269	0.81811
0.3987	0.85189	0.84761	0.84326	0.83885	0.83436
0.4799	0.86886	0.86471	0.86049	0.85620	0.85182
0.5600	0.88642	0.88244	0.87838	0.87424	0.87001
0.6407	0.90462	0.90087	0.89703	0.89310	0.88907
0.7201	0.92297	0.91953	0.91598	0.91232	0.90856
0.8000	0.94173	0.93872	0.93558	0.93231	0.92892
0.8801	0.96083	0.95838	0.95576	0.95299	0.95006
0.9603	0.98176	0.97982	0.97769	0.97539	0.97292
	T = 333.15 K	T = 338.15 K	T = 343.15 K	T = 348.15 K	T = 353.15 K
0.0800	0.76716	0.76224	0.75724	0.75217	0.74701
0.1581	0.78154	0.77667	0.77174	0.76672	0.76160
0.2401	0.79735	0.79256	0.78768	0.78271	0.77765
0.3206	0.81344	0.80871	0.80391	0.79900	0.79400
0.3987	0.82979	0.82513	0.82039	0.81556	0.81062
0.4799	0.84736	0.84281	0.83817	0.83344	0.82862
0.5600	0.86569	0.86128	0.85677	0.85218	0.84748
0.6407	0.88494	0.88072	0.87640	0.87197	0.86748
0.7201	0.90469	0.90071	0.89664	0.89245	0.88815
0.8000	0.92541	0.92177	0.91802	0.91414	0.91015
0.8801	0.94700	0.94379	0.94045	0.93697	0.93337
0.9603	0.97028	0.96750	0.96457	0.96150	0.95830

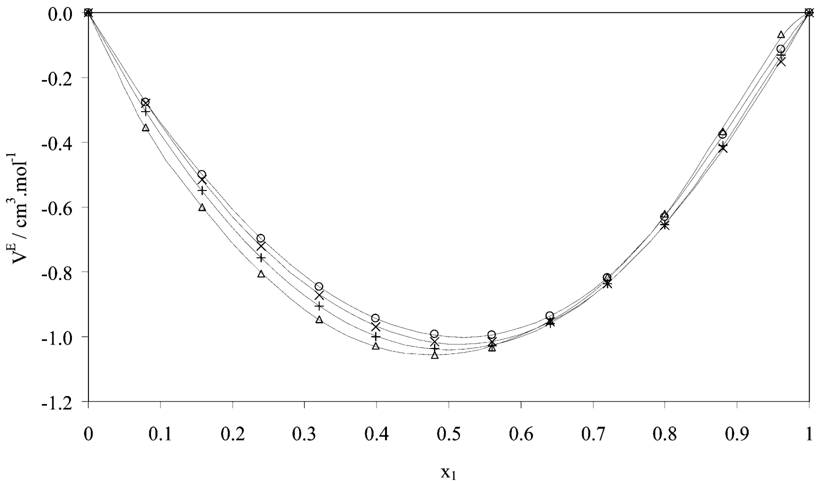

Figure 1. Excess molar volume (V^E) for H_2O (1) + MeOH (2) mixtures at various temperatures: ○, 283.15 K; ×, 303.15 K; +, 323.15 K; Δ, 343.15 K. Solid curves represent the values calculated with eq 5 and coefficients from Table 3.

Table 3. Values of Redlich−Kister Coefficients at Each Temperature for H_2O + MeOH Mixtures

T/K	A_0/cm^3·mol^{-1}	A_1/cm^3·mol^{-1}	A_2/cm^3·mol^{-1}	A_3/cm^3·mol^{-1}	A_4/cm^3·mol^{-1}	A_5/cm^3·mol^{-1}	σ/cm^6·mol^{-2}
283.15	−3.999	−0.302	0.085	0.218	0.833	0.836	0.00003
288.15	−4.024	−0.319	0.113	0.382	0.621	0.291	0.00006
293.15	−4.047	−0.314	0.125	0.462	0.475	−0.073	0.00008
298.15	−4.069	−0.299	0.121	0.492	0.388	−0.283	0.00009
303.15	−4.090	−0.266	0.105	0.465	0.338	−0.337	0.00009
308.15	−4.111	−0.219	0.082	0.378	0.328	−0.254	0.00007
313.15	−4.129	−0.160	0.044	0.256	0.369	−0.062	0.00004
318.15	−4.146	−0.090	0.001	0.105	0.437	0.235	0.00002
323.15	−4.163	−0.009	−0.043	−0.064	0.522	0.617	0.00001
328.15	−4.177	0.084	−0.106	−0.266	0.654	1.094	0.00004
333.15	−4.190	0.186	−0.167	−0.504	0.800	1.674	0.00011
338.15	−4.202	0.300	−0.236	−0.766	0.985	2.319	0.00024
343.15	−4.213	0.425	−0.321	−1.065	1.216	3.051	0.00044
348.15	−4.224	0.557	−0.388	−1.387	1.435	3.867	0.00074
353.15	−4.235	0.690	−0.464	−1.705	1.692	4.720	0.00117

The temperature dependence of the coefficients is given in Table 3 and can be represented by second-order polynomials (eqs 7 to 12).

$$A_0(T)/\text{cm}^3\cdot\text{mol}^{-1} = 2.3904 \times 10^{-6} \times (T/K)^2 - 0.018555 \times (T/K) - 0.6622 \quad (7)$$

$$A_1(T)/\text{cm}^3\cdot\text{mol}^{-1} = 0.0002329 \times (T/K)^2 - 0.13364 \times (T/K) + 18.8498 \quad (8)$$

$$A_2(T)/\text{cm}^3\cdot\text{mol}^{-1} = -0.0001579 \times (T/K)^2 + 0.09206 \times (T/K) - 13.3014 \quad (9)$$

$$A_3(T)/\text{cm}^3\cdot\text{mol}^{-1} = -\,0.0007004 \times (T/K)^2 + 0.41618 \times (T/K) - 61.3891 \quad (10)$$

$$A_4(T)/\text{cm}^3\cdot\text{mol}^{-1} = 0.0006784 \times (T/K)^2 - 0.41798 \times (T/K) + 64.7331 \quad (11)$$

$$A_5(T)/\text{cm}^3\cdot\text{mol}^{-1} = 0.0020808 \times (T/K)^2 - 1.26398 \times (T/K) + 191.7224 \quad (12)$$

The partial volume of each component ($\overline{V_i}$) is given by

$$\overline{V_i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} \quad (13)$$

Table 4. Partial Molar Volumes at Infinite Dilution in H_2O (1) + MeOH (2) Mixtures

T/K	$\overline{V_1^\infty}$/cm^3·mol^{-1}	$\overline{V_2^\infty}$/cm^3·mol^{-1}
283.15	14.2	37.7
288.15	14.4	37.3
293.15	14.6	37.1
298.15	14.6	37.1
303.15	14.6	37.2
308.15	14.5	37.4
313.15	14.4	37.8
318.15	14.2	38.3
323.15	14.0	38.9
328.15	13.7	39.6
333.15	13.4	40.4
338.15	13.0	41.3
343.15	12.6	42.3
348.15	12.1	43.3
353.15	11.7	44.5

We are interested in the volumetric properties of H_2O + MeOH because of the determination at each temperature of the partial volumes of H_2O at infinite dilution ($x_1 = 0$) in MeOH and of MeOH in H_2O ($x_2 = 0$). At infinite dilution, we have

$$\overline{V_1^\infty} = V_1^* + \sum A_n(-1)^n \; (x_1 = 0) \quad (14)$$

$$\overline{V_2^\infty} = V_2^* + \sum A_n \; (x_2 = 0) \quad (15)$$

The calculated partial molar volumes at infinite dilution are presented in Table 4.

Our results are compared to literature data. Experimental density values at three compositions (mole fractions of MeOH: 0.2034, 0.4002, and 0.8005) are available at 320

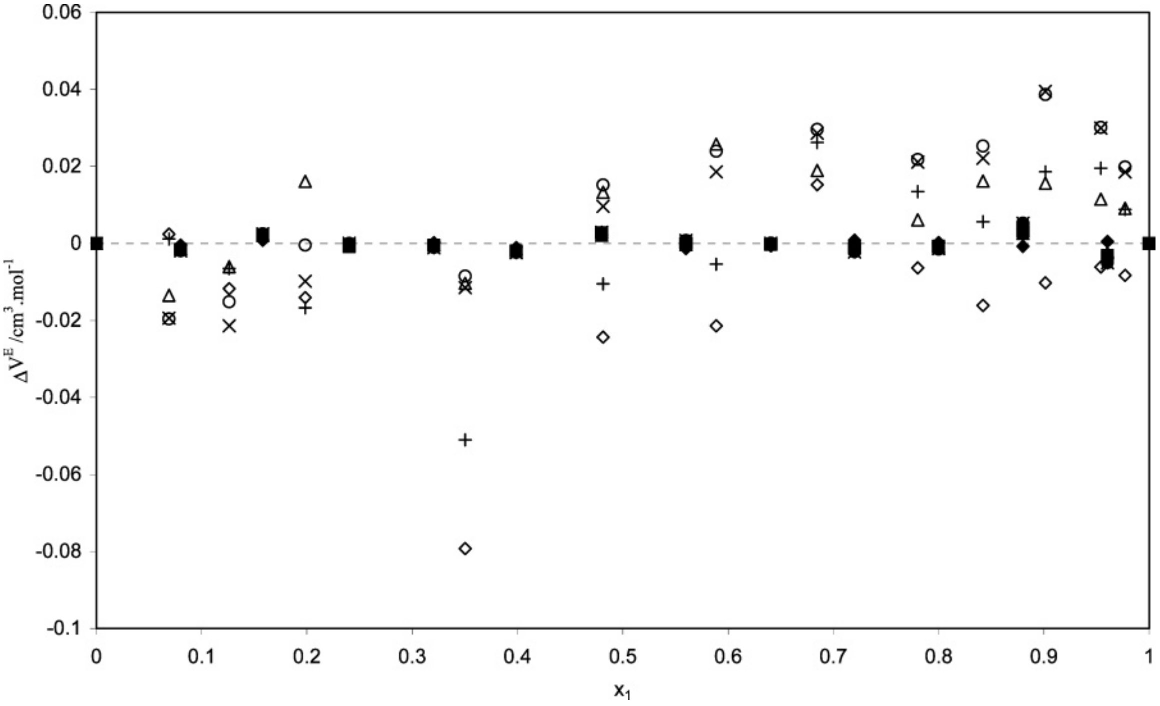

Figure 2. Deviation of our data and literature data (Dizechi and Marschall[10]) from the Redlich−Kister equation calculated data (parameters from Table 3) for H_2O (1) + MeOH (2) mixtures. Dizechi and Marschall: △, 283.15 K; ○, 293.15 K; ×, 303.15 K; +, 313.15 K; ◇, 323.15 K. This work: ▲, 283.15 K; ●, 293.15 K; *, 303.15 K; ■, 313.15 K; ◆, 323.15 K.

and 340 K from Yokoyama and Uematsu.[9] At 320 K, the density of pure MeOH from Yokoyama and Uematsu is 0.76535 g·cm^{-3}, a value very close to that calculated through eq 2: 0.7658 g·cm^{-3}. Safarov et al.[10] have determined excess volumes for three mole fractions of MeOH (0.25, 0.5, 0.75) at 298.15 and 323.15 K. Table 5 gives a comparison with our work (data calculated with the Redlich−Kister equation; see eqs 5 and 7−12). Dizechi and Marschall[11] have given density data at 5 temperatures for 12 compositions. Their pure-water densities are always higher than ours. Figure 2 is a deviation plot that compares our data and their data to calculated values through the Redlich−Kister equation (see eqs 5 and 7−12). In conclusion, we note that there is agreement between our data and those reported in the literature[9−11]

MEA + Methanol System. This binary system was studied in previous work.[5] The temperature dependence of the Redlich−Kister coefficients is given below (eqs 16 to 18).

$$A_0(T)/\mathrm{cm^3\cdot mol^{-1}} = -0.0001443 \times (T/K)^2 + 0.07398 \times (T/K) - 12.741 \quad (16)$$

$$A_1(T)/\mathrm{cm^3\cdot mol^{-1}} = 0.0001102 \times (T/K)^2 - 0.05761 \times (T/K) + 6.627 \quad (17)$$

$$A_2(T)/\mathrm{cm^3\cdot mol^{-1}} = -0.0002838 \times (T/K)^2 + 0.17170 \times (T/K) - 26.550 \quad (18)$$

Figure 3 presents the excess volumes at four temperatures for this binary system.

MEA + Water System. This binary system was studied by Maham et al.[2,3] and Lee and Lin.[4] There is some deviation between the two sources, notably for pure MEA. For example, at 303.15 K, Maham et al. give 1.00795 g·cm^{-3}, and Lee and Lin give 1.009 g·cm^{-3}. The study of the evolution of the Redlich−Kister (eq 5) parameters clearly shows two completely different tendencies. The Maham et al. data that correspond to a larger temperature range (more data) were preferred for parameter adjustment.

The temperature dependence of the parameters reported in Table 6 can be represented by second-order polynomials (eqs 19 to 24). The partial molar volumes at infinite dilution calculated using eqs 14 and 15 are reported in Table 7.

$$A_0(T)/\mathrm{cm^3\cdot mol^{-1}} = -6.9444 \times 10^{-5} \times (T/\mathrm{K})^2 + 0.04770 \times (T/\mathrm{K}) - 10.6351 \quad (19)$$

$$A_1(T)/\mathrm{cm^3\cdot mol^{-1}} = 4.7200 \times 10^{-6} \times (T/K)^2 - 0.00020 \times (T/K) - 0.9058 \quad (20)$$

$$A_2(T)/\mathrm{cm^3\cdot mol^{-1}} = -1.31579 \times 10^{-5} \times (T/K)^2 + 0.00803 \times (T/K) - 0.6853 \quad (21)$$

$$A_3(T)/\mathrm{cm^3\cdot mol^{-1}} = -2.7367 \times 10^{-4} \times (T/K)^2 + 0.16718 \times (T/K) - 24.6557 \quad (22)$$

$$A_4(T)/\mathrm{cm^3\cdot mol^{-1}} = -6.0622 \times 10^{-5} \times (T/K)^2 + 0.03372 \times (T/K) - 4.1802 \quad (23)$$

$$A_5(T)/\mathrm{cm^3\cdot mol^{-1}} = 2.6518 \times 10^{-4} \times (T/K)^2 - 0.16548 \times (T/K) + 25.8052 \quad (24)$$

Ternary System

Densities of H_2O (1) + MEA (2) + MeOH (3) mixtures were measured over the whole range of composition between 283.15 and 353.15 K. The studied compositions are reported in Table 8.

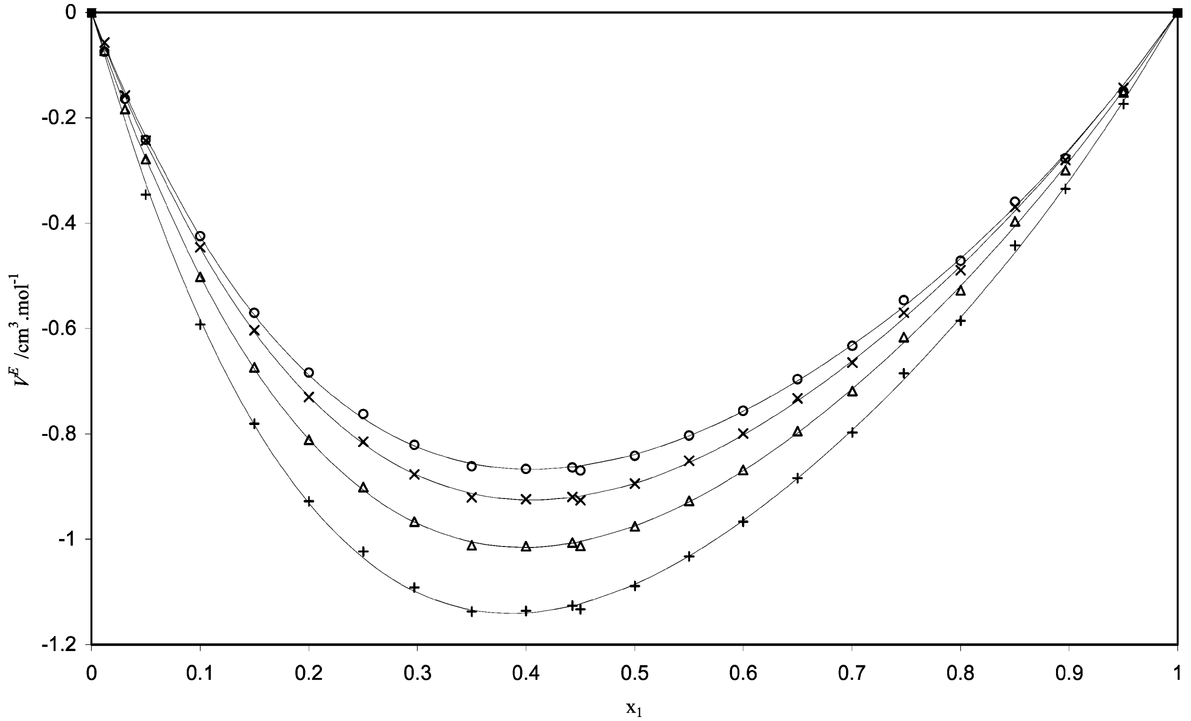

Figure 3. Excess molar volume (V^E) for MEA (1) + MeOH (2) mixtures at various temperatures. Experimental data are from Valtz et al.:[5] ○, 283.15 K; ×, 303.15 K; +, 323.15 K; △, 343.15 K. Solid curves represent the values calculated with eq 5 and coefficients from Valtz et al.[5]

Table 5. Comparison with Literature Data for H_2O (1) + MeOH (2) Mixtures

reference	T/K	x_1	d/g·cm^{-3}	V^E/cm^3·mol^{-1}	V^E/cm^3·mol^{-1} ^{a}	ΔV^E/cm^3·mol^{-1}
9	320	0.1995	0.80002	−0.675	−0.664	−0.011
	320	0.5998	0.88250	−0.894	−0.999	0.105
	320	0.7966	0.93397	−0.574	−0.655	0.081
	340	0.7966	0.92039	−0.660	−0.642	−0.018
10	298.15	0.25		−0.705	−0.735	0.030
	298.15	0.50		−1.014	−1.017	0.003
	298.15	0.75		−0.742	−0.771	0.029
	323.15	0.25		−0.738	−0.778	0.040
	323.15	0.50		−1.049	−1.040	−0.009
	323.15	0.75		−0.775	−0.775	0.000

[a] Calculated with the Redlich−Kister equation and parameters adjusted for our data.

The correlation (eq 2) with the parameters given in Table 1 is used to calculate the densities of each pure component.

Excess molar volumes, V^E, are calculated through eq 25 and reported in Table 9.

$$V^E = V - x_1V_1^* - x_2V_2^* - x_3V_3^* \qquad (25)$$

Excess molar volumes of the liquid ternary mixture can be calculated from excess molar volumes of binary systems weighted by λ_{ij} binary parameters (eq 26).

$$V^E = \lambda_{12}(T) \times V_{12}^E + \lambda_{13}(T) \times V_{13}^E + \lambda_{23}(T) \times V_{23}^E \qquad (26)$$

With this method, the excess volumes of binary mixtures are kept unchanged. The λ_{ij} parameters can be compared to binary interaction parameters; they take into account the proportion of binaries in the ternary excess molar volume and give an indication of interactions between the different molecules.

Table 10 gives the values of λ_{ij} as a function of temperature and the variance σ (see eq 6) of the excess molar volumes. The λ_{ij} parameters are temperature-dependent and can be well represented with a second-order polynomial (eqs 27 to 29).

$$\lambda_{12}(T) = 2.370 \times 10^{-5} \times (T/\text{K})^2 - 1.095 \times 10^{-2} \times (T/\text{K}) + 1.4055 \qquad (27)$$

$$\lambda_{13}(T) = 2.465 \times 10^{-6} \times (T/\text{K})^2 - 3.351 \times 10^{-3} \times (T/\text{K}) + 0.9906 \qquad (28)$$

$$\lambda_{23}(T) = -5.733 \times 10^{-7} \times (T/\text{K})^2 + 8.336 \times 10^{-5} \times (T/\text{K}) + 0.8374 \qquad (29)$$

Discussion

The excess molar volume V^E of liquid mixtures depends on the size and shape of the molecules and the intermo-

Table 6. Values of Redlich−Kister Coefficients at Each Temperature for H_2O + MEA Mixtures

T/K	A_0/cm^3·mol^{-1}	A_1/cm^3·mol^{-1}	A_2/cm^3·mol^{-1}	A_3/cm^3·mol^{-1}	A_4/cm^3·mol^{-1}	A_5/cm^3·mol^{-1}	σ/cm^6·mol^{-2}
278.15	−2.794	−0.783	0.524	1.430	0.447	−0.516	0.00015
288.15	−2.668	−0.562	0.537	0.734	0.447	0.156	0.00013
298.15	−2.574	−0.553	0.543	0.886	0.531	0.102	0.00002
303.15	−2.543	−0.544	0.537	0.956	0.522	−0.073	0.00003
313.15	−2.508	−0.500	0.543	0.860	0.417	−0.063	0.00003
333.15	−2.464	−0.440	0.531	0.578	0.268	0.196	0.00002
353.15	−2.443	−0.392	0.511	0.288	0.191	0.405	0.00007

Table 7. Partial Molar Volumes at Infinite Dilution in H_2O (1) + MEA (2) Mixtures

T/K	$\overline{V_1^\infty}$/$cm^3 \cdot mol^{-1}$	$\overline{V_2^\infty}$/$cm^3 \cdot mol^{-1}$
278.15	16.1	57.7
288.15	16.0	58.5
298.15	16.1	59.3
303.15	16.3	59.5
313.15	16.3	59.8
333.15	16.3	60.7
353.15	16.5	61.7

lecular forces. Geometrical packing effects, free volume effects, and strong specific interactions such as hydrogen bonding or dipole−dipole and dipole−induced dipole interactions considerably influence the V^E value in a fairly complex manner. All V^E values (for binary and ternary systems) are found to be negative, which is a characteristic of completely miscible (polar organic molecules with the possibility of hydrogen bonding) systems. The absolute value of V^E is an increasing function of temperature except for aqueous MEA. For the H_2O (1) + MeOH (3) and MEA (2) + MeOH (3) systems, this is due to packing effects, which are dominant. It is obvious that MEA or H_2O modifies the structure of MeOH and that this modification is enhanced by temperature. For aqueous MEA, temperature tends to reduce the number of H bonds.

Concerning the ternary system, the excess volume values are also negative, which signifies that this system is completely miscible. However, the behavior of different mixtures with respect to temperature is not identical. As an example, the excess volume decreases and then increases at higher temperatures for mixtures M3 (poor in MEA) and M23 (poor in water), whereas it decreases continually for mixtures M17 (poor in MeOH) and M15 (proportionally mixed). It is difficult to give an accurate interpretation of interactions occurring among the three species in the ternary system.

Table 8. Experimental Compositions for Density Measurements on H_2O (1) + MEA (2) + MeOH (3) Mixtures

mixture	x_1	x_2	mixture	x_1	x_2
M1	0.8585	0.0723	M13	0.1998	0.2359
M2	0.7722	0.0751	M14	0.5353	0.2633
M3	0.6483	0.0762	M15	0.3874	0.2856
M4	0.5864	0.0854	M16	0.2118	0.3122
M5	0.4721	0.0904	M17	0.4042	0.3576
M6	0.7130	0.1257	M18	0.2244	0.3971
M7	0.6087	0.1347	M19	0.2384	0.4922
M8	0.4857	0.1422	M20	0.8198	0.0738
M9	0.3514	0.1552	M21	0.2408	0.1780
M10	0.1914	0.1676	M22	0.4226	0.1496
M11	0.6355	0.1863	M23	0.6376	0.0836
M12	0.5116	0.2011	M24	0.1357	0.5601

Table 9. Densities (d) of H_2O (1) + MEA (2) + MeOH (3) Ternary Mixtures at Various Temperatures

mixture	d/$g \cdot cm^{-3}$	d/$g \cdot cm^{-3}$	d/$g \cdot cm^{-3}$	d/$g \cdot cm^{-3}$	d/$g \cdot cm^{-3}$	mixture	d/$g \cdot cm^{-3}$	d/$g \cdot cm^{-3}$	d/$g \cdot cm^{-3}$	d/$g \cdot cm^{-3}$	d/$g \cdot cm^{-3}$
	T = 283.15 K	T = 288.15 K	T = 293.15 K	T = 298.15 K	T = 303.15 K		T = 308.15 K	T = 313.15 K	T = 318.15 K	T = 323.15 K	T = 328.15 K
M1	0.99582	0.99387	0.99177	0.98953	0.98717	M13	0.89824	0.89402	0.88978	0.88549	0.88116
M2	0.97986	0.97725	0.97454	0.97172	0.96881	M14	0.97322	0.96945	0.96563	0.96177	0.95785
M3	0.95502	0.95176	0.94842	0.94502	0.94154	M15	0.94845	0.94448	0.94046	0.93641	0.93231
M4	0.94558	0.94210	0.93856	0.93495	0.93129	M16	0.92169	0.91755	0.91337	0.90916	0.90491
M5	0.92372	0.91996	0.91614	0.91227	0.90836	M17	0.96978	0.96587	0.96192	0.95794	0.95391
M6	0.98615	0.98318	0.98013	0.97700	0.97380	M18	0.94360	0.93952	0.93542	0.93127	0.92710
M7	0.96777	0.96438	0.96093	0.95742	0.95385	M19	0.96744	0.96343	0.95939	0.95532	0.95121
M8	0.94482	0.94111	0.93736	0.93357	0.92972	M20	0.97638	0.97352	0.97055	0.96746	0.96427
M9	0.92221	0.91828	0.91431	0.91031	0.90627	M21	0.88808	0.88385	0.87959	0.87528	0.87093
M10	0.89626	0.89212	0.88795	0.88376	0.87954	M22	0.91505	0.91101	0.90692	0.90278	0.89857
M11	0.98986	0.98656	0.98320	0.97980	0.97633	M23	0.93850	0.93483	0.93110	0.92728	0.92339
M12	0.96887	0.96525	0.96158	0.95787	0.95411	M24	0.96262	0.95854	0.95443	0.95031	0.94615
M13	0.91887	0.91480	0.91070	0.90657	0.90242		T = 333.15 K	T = 338.15 K	T = 343.15 K	T = 348.15 K	T = 353.15 K
M14	0.99139	0.98784	0.98424	0.98061	0.97693	M1	0.97029	0.96709	0.96374	0.96026	0.95676
M15	0.96778	0.96398	0.96014	0.95628	0.95238	M2	0.94918	0.94556	0.94183	0.93801	0.93410
M16	0.94200	0.93799	0.93395	0.92989	0.92581	M3	0.91901	0.91497	0.91084	0.90662	0.90231
M17	0.98883	0.98509	0.98130	0.97749	0.97365	M4	0.90781	0.90364	0.89938	0.89505	0.89062
M18	0.96362	0.95967	0.95568	0.95168	0.94766	M5	0.88359	0.87923	0.87479	0.87027	0.86566
M19	0.98717	0.98329	0.97935	0.97541	0.97144	M6	0.95290	0.94912	0.94527	0.94133	0.93730
M20	0.98890	0.98664	0.98425	0.98175	0.97912	M7	0.93105	0.92701	0.92288	0.91868	0.91440
M21	0.90870	0.90463	0.90054	0.89642	0.89226	M8	0.90549	0.90123	0.89691	0.89250	0.88814
M22	0.93456	0.93075	0.92688	0.92298	0.91904	M9	0.88106	0.87666	0.87220	0.86767	0.86306
M23	0.95571	0.95241	0.94903	0.94559	0.94208	M10	0.85343	0.84891	0.84432	0.83967	0.83497
M24	0.98273	0.97874	0.97474	0.97071	0.96667	M11	0.95423	0.95031	0.94632	0.94225	0.93812
	T = 308.15 K	T = 313.15 K	T = 318.15 K	T = 323.15 K	T = 328.15 K	M12	0.93051	0.92637	0.92216	0.91789	0.91355
M1	0.98466	0.98203	0.97928	0.97640	0.97340	M13	0.87679	0.87237	0.86788	0.86334	0.85875
M2	0.96579	0.96267	0.95945	0.95612	0.95270	M14	0.95387	0.94984	0.94574	0.94159	0.93737
M3	0.93798	0.93435	0.93063	0.92684	0.92297	M15	0.92816	0.92395	0.91969	0.91538	0.91100
M4	0.92755	0.92375	0.91988	0.91593	0.91191	M16	0.90062	0.89628	0.89189	0.88745	0.88295
M5	0.90438	0.90035	0.89626	0.89211	0.88788	M17	0.94984	0.94572	0.94155	0.93732	0.93304
M6	0.97052	0.96716	0.96371	0.96019	0.95658	M18	0.92288	0.91861	0.91431	0.90996	0.90556
M7	0.95022	0.94652	0.94276	0.93893	0.93503	M19	0.94707	0.94289	0.93867	0.93442	0.93011
M8	0.92583	0.92188	0.91787	0.91381	0.90968	M20	0.96096	0.95755	0.95404	0.95042	0.94670
M9	0.90219	0.89807	0.89390	0.88967	0.88540	M21	0.86652	0.86205	0.85753	0.85294	0.84827
M10	0.87529	0.87100	0.86668	0.86231	0.85790	M22	0.89431	0.88998	0.88558	0.88111	0.87657
M11	0.97281	0.96922	0.96557	0.96186	0.95808	M23	0.91941	0.91535	0.91121	0.90698	0.90267
M12	0.95031	0.94646	0.94256	0.93860	0.93458	M24	0.94197	0.93775	0.93349	0.92920	0.92487

Table 10. Values of λ_{ij} Binary Parameters[a]

T/K	λ_{12}	λ_{23}	λ_{13}	σ/cm^6·mol^{-2}
283.15	0.208	0.241	0.812	0.0006
288.15	0.219	0.230	0.813	0.0006
293.15	0.232	0.220	0.814	0.0005
298.15	0.246	0.210	0.813	0.0006
303.15	0.262	0.200	0.812	0.0006
308.15	0.280	0.191	0.810	0.0006
313.15	0.299	0.183	0.808	0.0006
318.15	0.321	0.174	0.806	0.0006
323.15	0.343	0.166	0.804	0.0006
328.15	0.367	0.157	0.801	0.0006
333.15	0.391	0.149	0.799	0.0006
338.15	0.416	0.140	0.798	0.0006
343.15	0.441	0.131	0.797	0.0006
348.15	0.466	0.122	0.798	0.0006
353.15	0.491	0.114	0.798	0.0006

[a] The standard deviation of λ_{ij} is 0.008.

Conclusions

In this paper, density values of the H_2O + MeOH and of the H_2O + MEA + MeOH systems were measured using the vibrating tube densimeter technique over the whole range of composition. These systems are completely miscible because the values of V^E are negative under the investigated conditions. A Redlich−Kister equation was used to correlate the excess volume of the binary systems. An expression of the density of the ternary is proposed on the basis of binary densities and specific binary interaction parameters determined directly from the ternary system densities.

Note Added after ASAP Posting. This article was posted ASAP 1/25/2005. Changes were made to the data in the last column of Table 2. This article was reposted 2/24/2005.

Literature Cited

(1) Amararene, F.; Balz, P.; Bouallou, C.; Cadours, R.; Lecomte, F.; Mougin, P.; Richon, D. Densities of Water + Diethanolamine + Methanol and Water + *N*-Methyldiethanolamine + Methanol at Temperatures Ranging from (283.15 to 353.15) K. *J. Chem. Eng. Data* **2003**, *48*, 1565−1570.

(2) Maham, Y.; Teng, T. T.; Hepler, L. G.; Mather, A. E. Volumetric properties of aqueous solutions of monoethanolamine, mono- and dimethylethanolamines at temperatures from 5 to 80 °C. *Thermochim. Acta* **2002**, *386*, 111−118.

(3) Maham, Y.; Teng, T. T.; Hepler, L. G.; Mather, A. E. Densities, Excess Molar Volumes, and Partial Molar Volumes for Binary Mixtures of Water with Monoethanolamine, Diethanolamine, and Triethanolamine from 25 to 80 °C *J. Solution Chem.* **1994**, *23*, 195−205.

(4) Lee, M. J.; Lin, T. K. Density and Viscosity for Monoethanolamine + Water, + Ethanol, and + 2-Propanol *J. Chem. Eng. Data* **1995**, *40*, 336−339.

(5) Valtz, A.; Coquelet, C.; Richon, D. Volumetric Properties of the Monoethanolamine-Methanol Mixture at Atmospheric Pressure from 283.15 to 353.15 K. *Thermochim. Acta,* in press.

(6) Machado, J. R. S.; Streett, W. B. Equation of State and Thermodynamic Properties of Liquid Methanol from 298 to 489 K and Pressures to 1040 bar. *J. Chem. Eng. Data* **1983**, *28*, 218−223.

(7) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987. (This reference is cited by Component Plus software from Prosim SA, version 3.1, 2002.)

(8) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

(9) Yokoyama, H.; Uematsu, M. Thermodynamic properties of {xCH_3-OH + (1-x)H_2O} at x=(1.0000, 0.8005, 0.4002, and 0.2034) in the temperature range from 320 K to 340 K at pressures up to 200 MPa. *J. Chem. Thermodyn.* **2003**, *35*, 813−823.

(10) Safarov, J.; Heydarov, S.; Shahverdiyev, A.; Hassel, E. Excess molar volumes V_m^E, isothermal compressibilities k, and thermal expansivities α of {(1-x)H2O+xCH3OH} at T=(298.15 to 523.15) K and pressures up to 60 MPa. *J. Chem. Thermodyn.* **2004**, *36*, 541−547.

(11) Dizechi, M.; Marschall, E. Viscosity of Some Binary and Ternary Liquid Mixtures. *J. Chem. Eng. Data* **1982**, *27*, 358−363.

Received for review August 26, 2004. Accepted December 5, 2004.

JE049691V