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Volumetric properties of the monoethanolamine–methanol mixture at atmospheric pressure from 283.15 to 353.15 K

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Abstract

Densities of the monoethanolamine–methanol binary mixture system were measured over the whole range of compositions at temperatures from 283.15 to 353.15 K using an Anton Paar digital vibrating glass tube densimeter. The density of this system has been found an increasing function of the monoethanolamine composition. The measured experimental excess volume data have been correlated using the Redlich–Kister equation. A set of parameters for the Redlich–Kister equation has been determined. Moreover, infinite dilution partial volumes were also calculated for each component.

Keywords: Binary system; Monoethanolamine; Density; Excess molar volume; Partial molar volume

1. Introduction

Monoethanolamine (MEA) is a widely used agent in carbon dioxide and hydrogen sulphide removal processes. This alkanolamine, generally combined with water, has been used in industry as a chemical solvent for a number of years. Aqueous alkanolamine solutions have however quite low efficiencies when used for the removal of other sulphur species, especially mercaptans. Combining a physical solvent to a chemical solvent is judicious for this type of removal purposes. Methanol is a good candidate.

Methanol (MeOH) is already used to remove acid gases from total gas stream. It is a physical solvent which is easily regenerated by heat. But, its cost is not negligible and its efficiency for acid gases removal is not as high as that obtained with chemical solvents. For simultaneous removal of both acid gases and non-acid sulphur compounds, mixtures of chemical and physical solvents, often referred to as "mixed" or "hybrid" solvents, have been developed. The presence of the physical solvent enhances the solution capacity [1]. Consequently, to design acid gas treatment equipment with the new solvents, industry needs new physicochemical data.

The main required data are: solubility data, kinetic data, and additionally: density, viscosity, etc. In this paper, we are concerned with densities of the MEA + MeOH binary mixture. Few publications are related to the densities of aqueous MEA solutions [2–4] but no about the MEA + MeOH binary system. Before thinking about modeling the MEA–H_2O–MeOH ternary mixture it is important to perform accurate modeling of the concerned binaries. It appears that the first step is getting accurate densities about the MEA + MeOH binary system.

In this work, densities of MEA + MeOH have been measured using a vibrating tube densimeter in the temperature range 283.15–353.15 K for the whole composition range. Excess molar volumes are represented using Redlich-Kister equation [5].

2. Experimental

Monoethanolamine [$H_2NC_2H_4OH$] was purchased from Aldrich with a certified GC purity >99% and methanol

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Nomenclature

A, B, C	parameters in Eq. (2)
A_n	Redlich–Kister parameters [$\text{cm}^3\,\text{mol}^{-1}$]
d	density [$\text{g}\,\text{cm}^{-3}$]
N_{exp}	number of experimental data
M_i	molar mass of pure component i [$\text{g}\,\text{mol}^{-1}$]
T	temperature [K]
T_{C}	critical temperature [K]
$\bar{V}_i$	partial volume of component i [$\text{cm}^3\,\text{mol}^{-1}$]
V_i^*	molar volume of pure component i [$\text{cm}^3\,\text{mol}^{-1}$]
x_i	liquid mole fraction of component i

Greek letters

σ	variance, see Eq. (6)
∞	infinite dilution state

Subscripts

cal	calculated
cor	correlation
1	MEA
2	MeOH
c	critical property

Superscript

E	excess property
*	pure compound

[CH_3OH] was obtained from Aldrich with a certified GC purity >99.93%. MEA and MeOH were carefully degassed before use and mixtures were prepared gravimetrically under a vacuum. The apparatus used in this work is an Anton Paar digital vibrating glass tube densimeter (model DMA5000), with a certified precision of $10^{-5}\,\text{g}\,\text{cm}^{-3}$. 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 with an accuracy of 0.01 K. The DMA5000 was calibrated at 293.15 K (for the determination of 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.

For the preparation and the charging of pure compounds and mixtures into the vibrating tube, the following procedure was applied to. Empty glass bottles of $20\,\text{cm}^3$ volume are air-tight closed with a septum and then evacuated with the help of a vacuum pump using a syringe needle introduced through the septum. Empty bottle is weighed, and then the less volatile component, freshly degassed by vacuum distillation, is introduced by means of a syringe. After weighing the bottle loaded with the first component, the more volatile one is added similarly and then the bottle is weighed again. All weighing are performed using a balance with an accuracy of 0.0003 g, therefore the average error in mole fraction is estimated to be better than 0.0003 ($\frac{\Delta x_i}{x_i} \leq 3\frac{\Delta m_i}{m_i}$, with m_i the weight of the component i and $\Delta m_i = 0.0003$ g the accuracy of the balance).

The above described preparation and loading procedure were used not only in order to determine the composition as exactly as possible, but also to prevent from formation of gas bubbles inside the vibrating tube; this happens frequently at high temperatures if the liquid is not well degassed. The maximum error of V^{E} is estimated to be less than $0.005\,\text{cm}^3\,\text{mol}^{-1}$.

3. Results

The densities of the pure MEA and pure MeOH were studied and compared with the values obtained with the correlation (Eq. (2)) mentioned by Reid et al. [6]:

$$d_{i,\text{cor}}^{*} = \frac{A}{B^{\left[1+\left(1-\frac{T}{T_{\text{C}}}\right)^{C}\right]}} \times \frac{M_i}{1000} \tag{2}$$

The A, B and C parameters are given in Table 1 the densities of pure MEA (MeOH) are presented in Table 2. The MEA (MeOH) parameters of Eq. (2) were obtained by fitting on MEA (MeOH) experimental densities and presented in Table 1. The MEA (MeOH) experimental densities and the calculated MEA (MeOH) densities through the correlation are available in Table 2. The deviation between MEA densities calculated from our parameters and MEA densities calculated from Reid et al. parameters is less than 0.07%.

The MeOH densities measured are in good agreement with the density mentioned by the supplier at 298.15 K. Several values of MeOH densities have been found in the literature. Villa et al. [7] give $0.78718\,\text{g}\,\text{cm}^{-3}$ at 298.15 K and compare this value to that of Carmona et al. [8] ($0.78669\,\text{g}\,\text{cm}^{-3}$). Uosaki et al. [9] give $0.78662\,\text{g}\,\text{cm}^{-3}$ at 298.15 K and $0.77238\,\text{g}\,\text{cm}^{-3}$ at 313.15 K. Our experimental values are in better agreement with all of these literature data than with data from the correlation proposed by Reid et al. This is the reason why we have adjusted the coefficients for the Eq. (2) on our MeOH experimental densities.

The densities of the mixture are reported in Tables 3–5. Three isothermal data (283.15, 318.15 and 353.15 K) are plotted in Fig. 1.

Table 1
Critical temperature for each component and parameters of Eq. (2)

Component	T_{C} (K)[b]	A ($\text{kmol}\,\text{m}^{-3}$)	B	C
MEA	678.20	1.0002[a]	0.2244[a]	0.2238[a]
MeOH	512.64	1.4791[a]	0.2176[a]	0.1971[a]
MEA	678.20	1.0010[b]	0.2250[b]	0.2150[b]
MeOH	512.64	2.2880[b]	0.2685[b]	0.2453[b]

[a] Values obtained from our experimental data.

[b] Values from [6].

Table 2
Density of pure MEA (MeOH) as a function of temperature

MEA						MeOH		
T (K)	d (g cm^{-3})	d_{cor} (g cm^{-3})	T (K)	d (g cm^{-3})	d_{cor} (g cm^{-3})	T (K)	d (g cm^{-3})	d_{cor} (g cm^{-3})
281.15	1.02555	1.02498	319.15	0.99540	0.99624	283.15	0.80067	0.80373
283.15	1.02399	1.02350	321.15	0.99379	0.99468	288.15	0.79599	0.79906
285.15	1.02242	1.02202	323.15	0.99219	0.99312	293.15	0.79129	0.79435
287.15	1.02084	1.02054	325.15	0.99058	0.99156	298.15	0.78658	0.78958
289.15	1.01926	1.01905	327.15	0.98896	0.98999	303.15	0.78186	0.78476
291.15	1.01768	1.01756	329.15	0.98734	0.98842	308.15	0.77710	0.77988
293.15	1.01610	1.01606	331.15	0.98572	0.98684	313.15	0.77232	0.77494
295.15	1.01452	1.01456	333.15	0.98410	0.98526	318.15	0.76752	0.76994
297.15	1.01294	1.01305	335.15	0.98248	0.98368	323.15	0.76267	0.76487
299.15	1.01135	1.01155	337.15	0.98085	0.98209	328.15	0.75777	0.75974
301.15	1.00976	1.01003	339.15	0.97921	0.98049	333.15	0.75283	0.75454
303.15	1.00817	1.00852	341.15	0.97758	0.97889			
305.15	1.00658	1.00700	343.15	0.97594	0.97728			
307.15	1.00499	1.00547	345.15	0.97430	0.97567			
309.15	1.00340	1.00394	347.15	0.97265	0.97406			
311.15	1.00180	1.00241	349.15	0.97099	0.97244			
313.15	1.00021	1.00087	351.15	0.96934	0.97082			
315.15	0.99860	0.99933	353.15	0.96768	0.96918			
317.15	0.99700	0.99779						

Excess molar volumes (see Fig. 2) are calculated by:

$$V^{E} = V - x_1 V_1^{*} - x_2 V_2^{*} \quad (3)$$

where V is the molar volume of the mixture MEA (1) + MeOH (2) see Tables 3–5. 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

$$V^{E} = \left[\frac{x_1 M_1 + x_2 M_2}{d}\right] - \frac{x_1 M_1}{d^{*}_{1,\mathrm{cor}}} - \frac{x_2 M_2}{d^{*}_{2,\mathrm{cor}}} \quad (4)$$

M_1 and M_2 are respectively the molar mass of MEA and MeOH. A Redlich–Kister equation (second order) was

Table 3
Densities (d) and molar excess volumes (V^{E}) for MEA (1) + MeOH (2) binary mixture at constant temperatures (283.15–303.15 K)

x_1	T = 283.15 K		T = 288.15 K		T = 293.15 K		T = 298.15 K		T = 303.15 K	
	d (g cm^{-3})	V^{E} (cm^3 mol^{-1})	d (g cm^{-3})	V^{E} (cm^3 mol^{-1})	d (g cm^{-3})	V^{E} (cm^3 mol^{-1})	d (g cm^{-3})	V^{E} (cm^3 mol^{-1})	d (g cm^{-3})	V^{E} (cm^3 mol^{-1})
0.0120	0.80583	−0.075	0.80117	−0.067	0.79649	−0.061	0.79180	−0.058	0.78710	−0.057
0.0310	0.81382	−0.164	0.80920	−0.159	0.80457	−0.157	0.79992	−0.156	0.79525	−0.157
0.0500	0.82145	−0.242	0.81686	−0.239	0.81226	−0.239	0.80764	−0.240	0.80300	−0.243
0.1000	0.84061	−0.425	0.83611	−0.427	0.83159	−0.431	0.82705	−0.438	0.82249	−0.446
0.1500	0.85827	−0.570	0.85379	−0.574	0.84933	−0.581	0.84486	−0.591	0.84037	−0.603
0.2002	0.87467	−0.684	0.87030	−0.693	0.86590	−0.703	0.86149	−0.715	0.85706	−0.730
0.2501	0.88965	−0.762	0.88533	−0.773	0.88098	−0.785	0.87662	−0.799	0.87224	−0.815
0.2974	0.90294	−0.821	0.89866	−0.832	0.89435	−0.845	0.89003	−0.860	0.88569	−0.877
0.3502	0.91672	−0.862	0.91248	−0.874	0.90821	−0.887	0.90394	−0.903	0.89965	−0.920
0.4001	0.92853	−0.866	0.92432	−0.878	0.92009	−0.892	0.91584	−0.906	0.91158	−0.924
0.4427	0.93812	−0.864	0.93394	−0.875	0.92973	−0.888	0.92551	−0.903	0.92128	−0.920
0.4502	0.93989	−0.869	0.93571	−0.881	0.93152	−0.894	0.92731	−0.909	0.92308	−0.926
0.5002	0.95016	−0.842	0.94601	−0.852	0.94184	−0.865	0.93766	−0.879	0.93346	−0.894
0.5501	0.95978	−0.803	0.95565	−0.813	0.95150	−0.823	0.94735	−0.836	0.94318	−0.851
0.6001	0.96889	−0.756	0.96479	−0.765	0.96067	−0.775	0.95654	−0.786	0.95239	−0.799
0.6501	0.97739	−0.696	0.97331	−0.703	0.96921	−0.712	0.96510	−0.721	0.96097	−0.733
0.7005	0.98559	−0.633	0.98153	−0.639	0.97745	−0.645	0.97337	−0.654	0.96928	−0.664
0.7479	0.99248	−0.546	0.98845	−0.551	0.98439	−0.556	0.98032	−0.562	0.97624	−0.570
0.8002	1.00019	−0.471	0.99618	−0.474	0.99215	−0.478	0.98811	−0.483	0.98406	−0.489
0.8502	1.00655	−0.359	1.00256	−0.360	0.99855	−0.362	0.99453	−0.365	0.99050	−0.369
0.8967	1.01263	−0.277	1.00866	−0.277	1.00466	−0.276	1.00067	−0.278	0.99666	−0.280
0.9501	1.01878	−0.149	1.01482	−0.146	1.01085	−0.144	1.00688	−0.143	1.00289	−0.143

Table 4
Densities (d) and molar excess volumes (V^E) for MEA (1) + MeOH (2) binary mixture at constant temperatures (308.15–328.15 K)

x_1	$T = 308.15$ K		$T = 313.15$ K		$T = 318.15$ K		$T = 323.15$ K		$T = 328.15$ K	
	d (g cm^{-3})	V^E (cm^3 mol^{-1})	d (g cm^{-3})	V^E (cm^3 mol^{-1})	d (g cm^{-3})	V^E (cm^3 mol^{-1})	d (g cm^{-3})	V^E (cm^3 mol^{-1})	d (g cm^{-3})	V^E (cm^3 mol^{-1})
0.0120	0.78238	−0.058	0.77763	−0.061	0.77284	−0.066	0.76802	−0.073	0.76316	−0.082
0.0310	0.79055	−0.160	0.78584	−0.166	0.78109	−0.174	0.77631	−0.184	0.77148	−0.195
0.0500	0.79835	−0.249	0.79366	−0.257	0.78895	−0.267	0.78419	−0.278	0.77940	−0.293
0.1000	0.81792	−0.457	0.81331	−0.469	0.80868	−0.485	0.80401	−0.502	0.79931	−0.521
0.1500	0.83587	−0.618	0.83133	−0.634	0.82677	−0.653	0.82217	−0.674	0.81754	−0.697
0.2002	0.85262	−0.747	0.84814	−0.766	0.84364	−0.787	0.83911	−0.811	0.83454	−0.836
0.2501	0.86783	−0.833	0.86341	−0.853	0.85896	−0.876	0.85448	−0.901	0.84996	−0.928
0.2974	0.88134	−0.896	0.87695	−0.917	0.87255	−0.941	0.86811	−0.967	0.86365	−0.995
0.3502	0.89533	−0.940	0.89100	−0.962	0.88663	−0.985	0.88225	−1.011	0.87783	−1.039
0.4001	0.90730	−0.943	0.90300	−0.964	0.89867	−0.987	0.89433	−1.013	0.88995	−1.040
0.4427	0.91702	−0.938	0.91275	−0.959	0.90845	−0.981	0.90414	−1.006	0.89979	−1.033
0.4502	0.91884	−0.945	0.91457	−0.965	0.91028	−0.988	0.90597	−1.012	0.90163	−1.039
0.5002	0.92924	−0.912	0.92500	−0.931	0.92074	−0.952	0.91646	−0.976	0.91215	−1.001
0.5501	0.93899	−0.867	0.93478	−0.885	0.93055	−0.905	0.92630	−0.927	0.92203	−0.950
0.6001	0.94822	−0.814	0.94404	−0.830	0.93984	−0.848	0.93562	−0.868	0.93137	−0.890
0.6501	0.95684	−0.746	0.95268	−0.761	0.94851	−0.777	0.94431	−0.795	0.94010	−0.815
0.7005	0.96516	−0.675	0.96103	−0.688	0.95689	−0.703	0.95272	−0.719	0.94853	−0.736
0.7479	0.97215	−0.579	0.96804	−0.590	0.96392	−0.602	0.95978	−0.616	0.95562	−0.631
0.8002	0.98000	−0.497	0.97592	−0.506	0.97182	−0.516	0.96771	−0.527	0.96357	−0.540
0.8502	0.98645	−0.374	0.98240	−0.381	0.97832	−0.388	0.97423	−0.396	0.97012	−0.406
0.8967	0.99263	−0.283	0.98860	−0.288	0.98455	−0.293	0.98048	−0.299	0.97639	−0.306
0.9501	0.99889	−0.144	0.99488	−0.146	0.99085	−0.148	0.98681	−0.152	0.98275	−0.156

applied for the excess molar volume:

$$V^E_{\mathrm{cal}} = x_1 x_2 \sum_i A_i (x_1 - x_2)^i \qquad (5)$$

with $i \leq 2$.

The Redlich–Kister coefficients (A_n) have been determined at each studied temperature and are presented in Table 6 along with the variance, σ, corresponding to each fit.

Table 5
Densities (d) and molar excess volumes (V^E) for MEA (1) + MeOH (2) binary mixture at constant temperatures (333.15–353.15 K)

x_1	$T = 333.15$ K		$T = 338.15$ K		$T = 343.15$ K		$T = 348.15$ K		$T = 353.15$ K	
	d (g cm^{-3})	V^E (cm^3 mol^{-1})	d (g cm^{-3})	V^E (cm^3 mol^{-1})	d (g cm^{-3})	V^E (cm^3 mol^{-1})	d (g cm^{-3})	V^E (cm^3 mol^{-1})	d (g cm^{-3})	V^E (cm^3 mol^{-1})
0.0120	0.75824	−0.092								
0.0310	0.76660	−0.208								
0.0500	0.77456	−0.308	0.76967	−0.226	0.76472	−0.250	0.75971	−0.276	0.75462	−0.303
0.1000	0.79456	−0.543	0.78976	−0.472	0.78491	−0.502	0.78000	−0.534	0.77502	−0.568
0.1500	0.81287	−0.722	0.80815	−0.661	0.80339	−0.696	0.79856	−0.731	0.79368	−0.770
0.2002	0.82994	−0.865	0.82528	−0.811	0.82058	−0.847	0.81583	−0.886	0.81102	−0.927
0.2501	0.84540	−0.957	0.84080	−0.910	0.83617	−0.948	0.83149	−0.988	0.82676	−1.031
0.2974	0.85914	−1.025	0.85460	−0.984	0.85000	−1.021	0.84536	−1.061	0.84069	−1.105
0.3502	0.87337	−1.069	0.86888	−1.034	0.86435	−1.072	0.85977	−1.112	0.85514	−1.154
0.4001	0.88553	−1.070	0.88108	−1.038	0.87660	−1.076	0.87207	−1.115	0.86750	−1.157
0.4427	0.89541	−1.061	0.89099	−1.034	0.88655	−1.070	0.88206	−1.108	0.87753	−1.148
0.4502	0.89726	−1.068	0.89286	−1.042	0.88842	−1.078	0.88394	−1.116	0.87942	−1.156
0.5002	0.90781	−1.028	0.90344	−1.005	0.89904	−1.039	0.89460	−1.074	0.89011	−1.112
0.5501	0.91772	−0.976	0.91338	−0.956	0.90901	−0.987	0.90462	−1.021	0.90018	−1.057
0.6001	0.92710	−0.914	0.92280	−0.897	0.91847	−0.926	0.91410	−0.957	0.90970	−0.990
0.6501	0.93585	−0.835	0.93159	−0.822	0.92729	−0.849	0.92296	−0.877	0.91860	−0.907
0.7005	0.94432	−0.755	0.94008	−0.744	0.93581	−0.767	0.93152	−0.793	0.92719	−0.820
0.7479	0.95143	−0.648	0.94722	−0.639	0.94298	−0.659	0.93872	−0.682	0.93442	−0.705
0.8002	0.95942	−0.554	0.95524	−0.548	0.95103	−0.565	0.94680	−0.584	0.94254	−0.604
0.8502	0.96599	−0.417	0.96184	−0.414	0.95766	−0.427	0.95346	−0.442	0.94923	−0.459
0.8967	0.97229	−0.315	0.96816	−0.314	0.96401	−0.325	0.95983	−0.336	0.95562	−0.348
0.9501	0.97867	−0.161	0.97457	−0.162	0.97045	−0.169	0.96630	−0.176	0.96212	−0.184

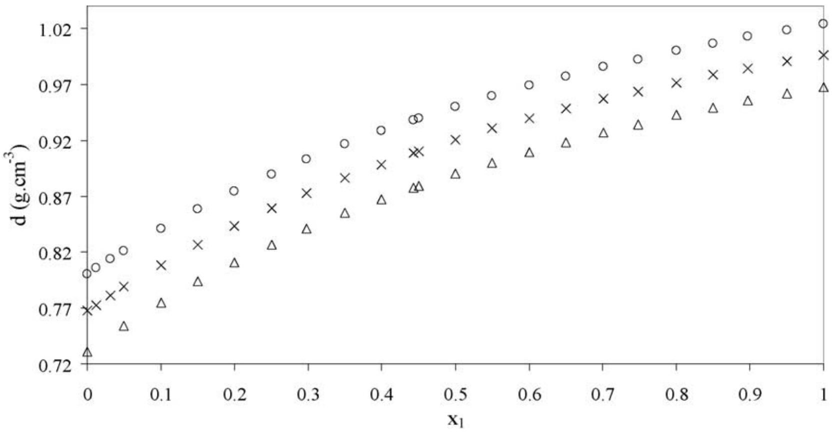

Fig. 1. Densities of MEA (1) + MeOH (2) at 283.15 K (◯), 318.15 K (×) and 353.15 K(△).

Table 6
Values of Redlich–Kister coefficients at each temperature

T (K)	A_0 ($cm^3 mol^{-1}$)	A_1 ($cm^3 mol^{-1}$)	A_2 ($cm^3 mol^{-1}$)	σ ($cm^6 mol^{-2}$)
283.15	−3.355	1.150	−0.705	0.00006
288.15	−3.404	1.171	−0.634	0.00004
293.15	−3.454	1.205	−0.597	0.00003
298.15	−3.512	1.243	−0.578	0.00003
303.15	−3.576	1.287	−0.573	0.00003
308.15	−3.646	1.337	−0.586	0.00003
313.15	−3.723	1.390	−0.612	0.00003
318.15	−3.807	1.450	−0.653	0.00003
323.15	−3.899	1.515	−0.704	0.00003
328.15	−3.999	1.586	−0.772	0.00004
333.15	−4.104	1.661	−0.855	0.00006
338.15	−4.219	1.741	−0.947	0.00006
343.15	−4.341	1.831	−1.052	0.00008
348.15	−4.472	1.923	−1.170	0.00011
353.15	−4.612	2.025	−1.298	0.00014

$$\sigma = \left[\sum \frac{(V^{E} - V^{E}_{cal})^2}{N_{exp} - 3}\right] \tag{6}$$

The temperature dependency of coefficients given in Table 6 can be represented by second order polynomials (Eqs. (7)–(9)):

$$A_0(T) = -0.0001443 \times T^2 + 0.07398 \times T - 12.741 \tag{7}$$

$$A_1(T) = 0.0001102 \times T^2 - 0.05761 \times T + 6.627 \tag{8}$$

$$A_2(T) = -0.0002838 \times T^2 + 0.17170 \times T - 26.550 \tag{9}$$

The partial volume of each component ($\bar{V}_i$) is given by

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} \tag{10}$$

After deriving Eq. (3) with respect to n_i and combining the result to Eq. (10) leads to equations for the partial molar

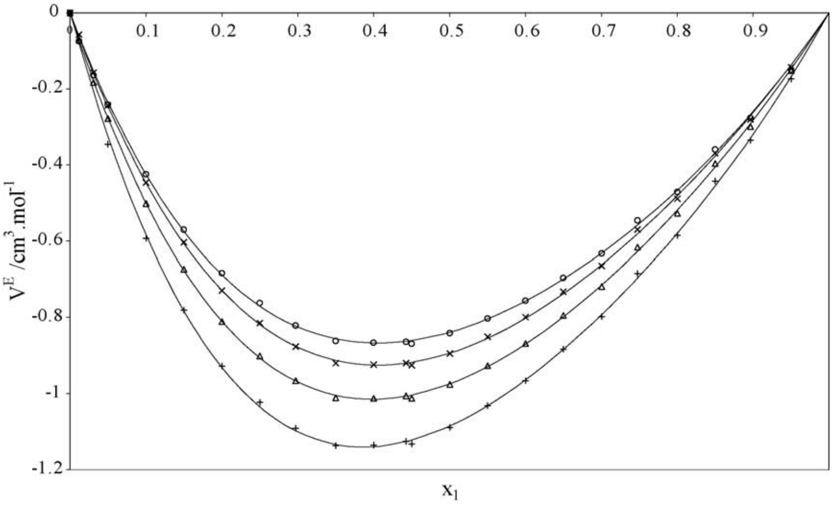

Fig. 2. Excess molar volume (V^E) for the MEA (1) + MeOH (2) binary system at constant temperatures. (◯) 283.15 K, (×) 303.15 K, (+) 323.15 K, (△) 343.15 K. Solid curves represent the values calculated from Eq. (3) with coefficients from Table 6.

Table 7
Partial molar volumes at infinite dilution and partial molar excess volumes at infinite dilution in the MEA (1)–MeOH (2) mixture

T (K)	$\bar{V}_1^\infty$ (cm^3 mol^{-1})	$\bar{V}_2^\infty$ (cm^3 mol^{-1})	$(\bar{V}_1^\mathrm{E})^\infty$ (cm^3 mol^{-1})	$(\bar{V}_2^\mathrm{E})^\infty$ (cm^3 mol^{-1})
283.15	54.5	37.1	−3.5	−2.3
288.15	54.7	37.4	−3.6	−2.3
293.15	54.9	37.6	−3.7	−2.3
298.15	55.0	37.9	−3.8	−2.3
303.15	55.2	38.1	−4.0	−2.4
308.15	55.3	38.3	−4.2	−2.4
313.15	55.3	38.5	−4.4	−2.5
318.15	55.4	38.7	−4.6	−2.6
323.15	55.4	38.9	−4.9	−2.7
328.15	55.5	39.1	−5.2	−2.8
333.15	55.4	39.3	−5.5	−2.9
338.15	55.4	39.4	−5.8	−3.1
343.15	55.4	39.6	−6.2	−3.2
348.15	55.3	39.8	−6.6	−3.4
353.15	55.2	39.9	−7.0	−3.6

volume of MEA and MeOH:

$$\bar{V}_1 = V^\mathrm{E} + V_1^* - x_2\left(\frac{\partial V^\mathrm{E}}{\partial x_2}\right)_{T,P} \tag{11}$$

$$\bar{V}_2 = V^\mathrm{E} + V_2^* - x_1\left(\frac{\partial V^\mathrm{E}}{\partial x_1}\right)_{T,P} \tag{12}$$

By using the differentiation of the Redlich–Kister equation (Eq. (5)) with respect to x_2 and substitution in Eqs. (11) and (12), the expression of partial molar volumes (Eqs. (13) and (14)) are obtained:

$$\bar{V}_1 = V_1^* + x_2^2\sum A_n(1-2x_2)^n + 2x_2^2(1-x_2)\sum nA_n(1-2x_2)^{n-1} \tag{13}$$

$$\bar{V}_2 = V_2^* + (1-x_2)^2\sum A_n(1-2x_2)^n - 2x_2(1-x_2)^2\sum nA_n(1-2x_2)^{n-1} \tag{14}$$

An interest in the volumetric properties of MEA + MeOH is the determination at each temperature of the partial volumes of alkanolamine at infinite dilution ($x_2 = 0$) in MeOH and of MeOH in MEA ($x_1 = 0$). At infinite dilution, Eqs. (13) and (14) are transformed into Eqs. (15) and (16):

$$\bar{V}_1^\infty = V_1^* + \sum A_n(-1)^n \quad (x_1 = 0) \tag{15}$$

$$\bar{V}_2^\infty = V_2^* + \sum A_n \quad (x_2 = 0) \tag{16}$$

The calculated partial molar volumes at infinite dilution and the partial molar excess volumes at infinite dilution (Eqs. (17) and (18)) are presented in Table 7:

$$(\bar{V}_1^\mathrm{E})^\infty = \sum A_n(-1)^n \quad (x_1 = 0) \tag{17}$$

$$(\bar{V}_2^\mathrm{E})^\infty = \sum A_n \quad (x_2 = 0) \tag{18}$$

4. Discussion

The excess molar volume V^E of liquid mixtures depends on the size and shape of the molecules and the intermolecular forces. Geometrical packing effects, free volume effects, and strong specific interactions like hydrogen bonding or dipole–dipole and dipole-induced dipole interactions, influence considerably the V^E value in a fairly complex manner. All our V^E values are negative, a characteristic of completely miscible (two polar organic molecules with the possibility of hydrogen bonding) systems. The same trend was observed with the system water + ethanolamine [10]. The absolute value of V^E is an increasing function of temperature. It is due to the packing effects which become dominant. This phenomenon was yet observed in a previous study concerning alcohol + triethylene glycol systems [11]. It has been also described in literature for 1-alkanol + hexane systems [12], 1-alkanol + nonane systems [13] and 1-hexanol + ether systems [14].

The partial molar volume at infinite dilution of MEA and MeOH is not very dependent on temperature except for MEA which exhibits a slight maximum at 328.15 K. The partial molar volumes at infinite dilution of MEA ($x_2 = 0$) are smaller than the corresponding molar volumes of the pure alkanolamine, V_2^* (the partial molar excess volume is negative at infinite dilution). It could indicate that the alkanolamine molecules are partially packed inside the open or empty space left in liquid MeOH. There is a few change in the structure of liquid MeOH. Also, the partial molar volumes of MeOH are smaller than the corresponding molar volumes of the pure MeOH, V_1^*. This confirms the existence of hydrogen bondings which create an “empty” volume in liquid MeOH.

5. Conclusion

In this paper, densities values of the MEA (1) + MeOH (2) were measured by the vibrating tube densimeter technique in the whole range of composition. This system is completely miscible as the values of V^E are negative. The partial volumes at infinite dilution were also determined by using the Redlich–Kister equation used to correlate the excess volume of the binary system.

References

[1] F. Amararene, P. Balz, C. Bouallou, R. Cadours, F. Lecomte, P. Mougin, D. Richon, J. Chem. Eng. Data 48 (2003) 1565–1570.
[2] Y. Maham, T.T. Teng, L.G. Hepler, A.E. Mather, Thermochim. Acta 386 (2002) 111–118.
[3] M.J. Lee, T.K. Lin, J. Chem. Eng. Data 40 (1995) 336–339.
[4] Y. Maham, T.T. Teng, L.G. Hepler, A.E. Mather, J. Solution Chem. 23 (1994) 195–205.
[5] O. Redlich, A.T. Kister, Ind. Eng. Chem. 40 (1948) 345–348.
[6] R.C. Reid, J.M. Prausnitz, B.E. Boiling, The Properties of Gases and Liquids, 4th ed., McGraw-Hill, New York, 1987.

[7] S. Villa, N. Riesco, I. Garcia de la Fuente, J.A. Gonzalez, J.C. Cobos, Fluid Phase Equilib. 198 (2002) 313–329.
[8] F.J. Carmona, F.J. Arrayo, I. Garcia de la Fuente, J.A. Gonzalez, J.C. Cobos, Can. J. Chem. 77 (1999) 1608–1616.
[9] Y. Uosaki, T. Hamaguchi, T. Moriyoshi, Fluid Phase Equilib. 136 (1997) 299–306.
[10] U.R. Kapadi, D.G. Hundiwale, N.B. Patil, M.K. Lande, Fluid Phase Equilib. 201 (2002) 335–341.
[11] A. Valtz, M. Teodorescu, I. Wichterle, D. Richon, Fluid Phase Equilib. 215 (2004) 129–142.
[12] A. Heintz, B. Schmittecker, D. Wagner, R.N. Lichtenthaler, J. Chem. Eng. Data 31 (1986) 487–492.
[13] D. Wagner, A. Heintz, J. Chem. Eng. Data 31 (1986) 483–487.
[14] S. Villa, N. Riesco, F.J. Carmona, I. Garcia de la Fuente, J.A. Gonzalez, J.C. Cobos, Thermochim. Acta 362 (2000) 169–177.