

# Volumetric properties of aqueous solutions of monoethanolamine, mono- and dimethylethanolamines at temperatures from 5 to 80 °C I

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## Abstract

Densities of aqueous binary mixtures of monoethanolamine, monomethylethanolamine and dimethylethanolamine were measured over the whole range of compositions at temperatures varying from 5 to 80 °C. The density of monoethanolamine + water mixtures shows a maximum ( $x_2 = 0.43$  at 5 °C). The density behavior of monoethanolamine + water and dimethylethanolamine + water mixtures is different from the monoethanolamine + water system. The composition dependence of the densities of these two mixtures was classified in two distinct zones. This separation line occurs at  $x_2 = 0.20$  for monoethanolamine + water and  $x_2 = 0.12$  for the dimethylethanolamine + water system. In the low concentration zone, the density values exhibit a minimum and a maximum at increasing ethanolamine concentration, while in the high concentration zone, the density values approach the density of the pure alkanolamine in a monotonic fashion. The excess molar volume of these mixtures is dependent on the structure of the ethanolamines:  $V^E(\text{monoethanolamine} + \text{water}) < V^E(\text{monoethanolamine} + \text{water}) < V^E(\text{dimethylethanolamine} + \text{water})$ . © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Binary aqueous systems; Monoethanolamine; Monomethylethanolamine; Dimethylethanolamine; Density; Excess molar volume; Partial molar volume

## 1. Introduction

This is a continuation of our effort to collect physical (volumetric and transport) and thermodynamic properties of pure alkanolamines and their aqueous solutions. Densities, excess molar volumes and excess molar enthalpies of binary monoethanolamine, MEA + water; monomethylethanolamine, MMEA + water;

and dimethylethanolamine, DMEA + water have been reported at 25 °C [2]. Densities, isobaric specific heat capacities and isentropic compressibilities were measured in the monoethanolamine, MEA + H<sub>2</sub>O system at temperatures from 10 to 40 °C [3]. The volumetric properties of the ethanolamine, MEA + water; diethanolamine, DEA + water; and triethanolamine, TEA + water systems [4] and methyldiethanolamine, MDEA + water and ethyldiethanolamine, EDEA + water systems [5] have been given from 25 to 80 °C. Recently, densities and excess molar volumes of dimethylethanolamine, DMEA + water and diethylethanolamine, DEEA + water were also reported at 20–40 °C [6]. Transport properties of pure ethanolamines were given

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DiGuilio et al. [7,9] and those of diethanolamine, DEA + water and methyldiethanolamine, MDEA + water systems were presented [8]. The specific heat capacities of pure liquid alkanolamines [10] and excess molar enthalpies of the diethanolamine, DEA + water; methyldiethanolamine, MDEA + water; and triethanolamine, TEA + water systems at 25 °C [11] and of monoethylethanolamine, MEEA + water; diethylethanolamine, DEEA + water; mono-*n*-propylethanolamine, *n*-PEA + water; and 2-amino-2-methyl-1-propanol, AMP + water systems at 25 °C [12] and of diethanolamine, DEA + H<sub>2</sub>O at 45–65 °C; methyldiethanolamine, MDEA + H<sub>2</sub>O at 65 °C and ethyldiethanolamine, EDEA + H<sub>2</sub>O and *n*-butyldiethanolamine, *n*-BDEA + H<sub>2</sub>O systems at 25–65 °C [13] have been measured.

Here, we report the volumetric properties of the system (monoethanolamine, MEA + H<sub>2</sub>O) at 5 and 15 °C and the monomethylethanolamine, MMEA + water and dimethylethanolamine, DMEA + water systems at temperatures between 5 and 80 °C. The properties of aqueous solutions of monoethylethanolamine, MEEA and diethylethanolamine, DEEA will be given in a separate paper in this journal [1].

## 2. Experimental

Monoethanolamine [H<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>OH, MEA, 99%], was obtained from Fisher Scientific, and monomethylethanolamine [CH<sub>3</sub>HNC<sub>2</sub>H<sub>4</sub>OH, MMEA, 99%] and dimethylethanolamine [(CH<sub>3</sub>)<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>OH, DMEA, 99%] were obtained from Aldrich Chemical. These compounds were used as received, after confirmatory analysis by titration with standard hydrochloric acid. Mixtures of these ethanolamines with nano-pure distilled water were made by weighing (an absolute accuracy of  $1 \times 10^{-4}$ ) with care being taken to minimize exposure to air (carbon dioxide). The details of the measurements have been given earlier [4].

## 3. Results

The densities and excess molar volumes of the MEA + H<sub>2</sub>O, MMEA + H<sub>2</sub>O and DMEA + H<sub>2</sub>O mixtures are given in Tables 1–3, respectively. Our density values are in excellent agreement with the

Table 1  
Densities (g/cm<sup>3</sup>) and excess molar volumes (cm<sup>3</sup>/mol) of (monoethanolamine, MEA + H<sub>2</sub>O) mixtures at 5 and 15 °C

$x_2$	5 °C		15 °C	
	$d$	$V^E$	$d$	$V^E$
0.0000	0.99996	–	0.99910	–
0.0054	1.00105	–0.011	0.99996	–0.009
0.0148	1.00285	–0.029	1.00143	–0.025
0.0230	1.00444	–0.046	1.00267	–0.039
0.0313	1.00587	–0.061	1.00389	–0.053
0.0495	1.00915	–0.099	1.00645	–0.085
0.0674	1.01193	–0.133	1.00905	–0.121
0.0875	1.01518	–0.178	1.01184	–0.164
0.1102	1.01876	–0.233	1.01495	–0.216
0.1626	1.02593	–0.357	1.02124	–0.337
0.2322	1.03320	–0.506	1.02745	–0.479
0.3032	1.03788	–0.620	1.03088	–0.575
0.4194	1.04098	–0.708	1.03344	–0.668
0.4653	1.04089	–0.705	1.03343	–0.676
0.5382	1.04014	–0.676	1.03245	–0.650
0.6220	1.03863	–0.610	1.03075	–0.589
0.7228	1.03629	–0.494	1.02817	–0.475
0.7958	1.03428	–0.382	1.02607	–0.367
0.8446	1.03285	–0.296	1.02462	–0.285
0.9336	1.03045	–0.135	1.02213	–0.130
0.9660	1.02955	–0.071	1.02120	–0.067
1.0000	1.02860	–	1.02025	–

values at the temperatures that were measured by others [2,3,6]. The densities of MEA + H<sub>2</sub>O mixtures have a maximum at  $x_2 = 0.425$  at 5 °C, and its position moves toward a lower mole fraction of ethanolamine at increasing temperatures ( $x_2$  (maximum) = 0.30 at 80 °C) [3]. The densities of MMEA + H<sub>2</sub>O and DMEA + H<sub>2</sub>O mixtures show a different composition dependence from the MEA + H<sub>2</sub>O system. The density behavior of MMEA + H<sub>2</sub>O mixtures at different temperatures is shown in Fig. 1. One may classify this behavior of densities in two different zones, at  $x_2 = 0.20$  for MMEA + H<sub>2</sub>O and  $x_2 = 0.12$  for DMEA + H<sub>2</sub>O mixtures, where at lower mole fractions the variation of the density is peculiar. It decreases and passes through a minimum; then it passes through a maximum. At higher concentrations, it decreases smoothly to the density of the pure alkanolamines.

This peculiar behavior of density against the mole fraction of alkanolamines is also temperature-dependent (Fig. 1). The density variation is more pronounced at lower temperature and it disappears

Table 2

Densities (g/cm<sup>3</sup>) and excess molar volumes (cm<sup>3</sup>/mol) of (monomethylethanolamine, MMEA + H<sub>2</sub>O) mixtures at temperatures from 5 to 80 °C

$x_2$	5 °C		15 °C		25 °C		30 °C		40 °C		60 °C		80 °C	
	$d$	$V^E$	$d$	$V^E$	$d$	$V^E$	$d$	$V^E$	$d$	$V^E$	$d$	$V^E$	$d$	$V^E$
0.0000	0.99996	–	0.99910	–	0.99704	–	0.99565	–	0.99222	–	0.98320	–	0.97180	–
0.0048	0.99980	–0.015	0.99885	–0.017	0.99680	–0.019	0.99532	–0.018	0.99172	–0.017	0.98264	–0.019	0.97121	–0.021
0.0086	0.99972	–0.028	0.99868	–0.030	0.99659	–0.034	0.99507	–0.033	0.99155	–0.034	0.98229	–0.036	0.97085	–0.041
0.0131	0.99972	–0.046	0.99860	–0.049	0.99638	–0.052	0.99482	–0.051	0.99106	–0.049	0.98204	–0.059	0.97024	–0.059
0.0188	0.99980	–0.069	0.99852	–0.072	0.99622	–0.076	0.99465	–0.077	0.99081	–0.074	0.98154	–0.085	0.96973	–0.087
0.0261	1.00021	–0.105	0.99860	–0.106	0.99613	–0.110	0.99449	–0.111	0.99023	–0.102	0.98063	–0.111	0.96915	–0.125
0.0411	1.00129	–0.184	0.99918	–0.183	0.99622	–0.185	0.99440	–0.185	0.98981	–0.172	0.97988	–0.187	0.96783	–0.197
0.0561	1.00278	–0.274	1.00001	–0.267	0.99655	–0.264	0.99449	–0.262	0.99023	–0.260	0.97906	–0.259	0.96642	–0.264
0.0768	1.00486	–0.403	1.00134	–0.390	0.99713	–0.378	0.99482	–0.374	0.99023	–0.370	0.97790	–0.357	0.96477	–0.360
0.0935	1.00652	–0.510	1.00213	–0.484	0.99754	–0.470	0.99507	–0.465	0.98981	–0.448	0.97715	–0.437	0.96345	–0.435
0.1425	1.00968	–0.796	1.00391	–0.755	0.99804	–0.725	0.99482	–0.708	0.98932	–0.693	0.97409	–0.642	0.95940	–0.632
0.1993	1.00943	–1.037	1.00283	–0.990	0.99605	–0.947	0.99254	–0.928	0.98646	–0.904	0.96996	–0.838	0.95429	–0.816
0.2799	1.00453	–1.224	0.99736	–1.178	0.99008	–1.132	0.98658	–1.119	0.98023	–1.094	0.96298	–1.024	0.94646	–0.988
0.3524	0.99806	–1.274	0.99081	–1.238	0.98346	–1.199	0.97966	–1.179	0.97329	–1.157	0.95618	–1.107	0.93939	–1.069
0.4103	0.99251	–1.257	0.98527	–1.231	0.97784	–1.195	0.97415	–1.182	0.96776	–1.162	0.95047	–1.113	0.93373	–1.083
0.4553	0.98837	–1.224	0.98097	–1.198	0.97363	–1.170	0.96975	–1.150	0.96338	–1.133	0.94623	–1.097	0.92954	–1.072
0.5505	0.97969	–1.081	0.97239	–1.074	0.96497	–1.050	0.96087	–1.021	0.95493	–1.029	0.93780	–1.007	0.92119	–0.990
0.6562	0.97136	–0.874	0.96374	–0.863	0.95641	–0.852	0.95245	–0.832	0.94655	–0.849	0.92954	–0.845	0.91285	–0.826
0.7295	0.96601	–0.691	0.95835	–0.685	0.95115	–0.688	0.94735	–0.679	0.94132	–0.691	0.92454	–0.710	0.90785	–0.692
0.8186	0.96058	–0.473	0.95305	–0.487	0.94548	–0.470	0.94147	–0.448	0.93566	–0.479	0.91894	–0.512	0.90241	–0.506
0.8825	0.95709	–0.308	0.94956	–0.329	0.94183	–0.303	0.93778	–0.278	0.93205	–0.319	0.91513	–0.342	0.89882	–0.354
0.9584	0.95345	–0.114	0.94559	–0.116	0.93805	–0.109	0.93409	–0.092	0.92811	–0.116	0.90883	–0.120	0.89460	–0.132
1.0000	0.95155	–	0.94362	–	0.93614	–	0.93238	–	0.92610	–	0.90883	–	0.89240	–

Table 3

Densities (g/cm<sup>3</sup>) and excess molar volumes (cm<sup>3</sup>/mol) of (dimethylethanolamine, DMEA + H<sub>2</sub>O) mixtures at temperatures from 5 to 80 °C

$x_2$	5 °C		15 °C		25 °C		30 °C		40 °C		60 °C		80 °C	
	$d$	$V^E$	$d$	$V^E$	$d$	$V^E$	$d$	$V^E$	$d$	$V^E$	$d$	$V^E$	$d$	$V^E$
0.0000	0.99996	–	0.99910	–	0.99704	–	0.99565	–	0.99222	–	0.98320	–	0.97180	–
0.0059	0.99897	–0.041	0.99786	–0.041	0.99563	–0.042	0.99424	–0.044	0.99072	–0.046	0.98146	–0.049	0.96990	–0.052
0.0111	0.99839	–0.081	0.99686	–0.078	0.99472	–0.085	0.99316	–0.085	0.98956	–0.089	0.98013	–0.095	0.96820	–0.097
0.0209	0.99773	–0.165	0.99603	–0.166	0.99327	–0.168	0.99150	–0.168	0.98765	–0.173	0.97769	–0.180	0.96531	–0.183
0.0334	0.99756	–0.284	0.99504	–0.278	0.99182	–0.280	0.98993	–0.281	0.98563	–0.285	0.97492	–0.291	0.96196	–0.293
0.0462	0.99781	–0.415	0.99462	–0.404	0.99074	–0.400	0.98852	–0.398	0.98376	–0.399	0.97219	–0.400	0.95862	–0.400
0.0600	0.99831	–0.562	0.99421	–0.540	0.98942	–0.524	0.98711	–0.524	0.98186	–0.521	0.96930	–0.513	0.95516	–0.512
0.0771	0.99847	–0.734	0.99354	–0.703	0.98817	–0.682	0.98529	–0.674	0.97937	–0.664	0.96591	–0.650	0.95046	–0.628
0.1145	0.99665	–1.055	0.99053	–1.013	0.98387	–0.976	0.98040	–0.960	0.97326	–0.933	0.95837	–0.911	0.94194	–0.886
0.1621	0.99151	–1.365	0.98419	–1.307	0.97659	–1.259	0.97280	–1.241	0.96517	–1.214	0.94869	–1.172	0.93105	–1.131
0.2259	0.98167	–1.618	0.97378	–1.558	0.96570	–1.510	0.96175	–1.494	0.95364	–1.465	0.93633	–1.422	0.91813	–1.381
0.3160	0.96683	–1.764	0.95892	–1.723	0.95072	–1.686	0.94658	–1.670	0.93828	–1.647	0.92049	–1.610	0.90169	–1.560
0.3780	0.95745	–1.777	0.94945	–1.743	0.94112	–1.707	0.93703	–1.698	0.92870	–1.682	0.91078	–1.651	0.89188	–1.601
0.4361	0.94916	–1.726	0.94141	–1.715	0.93293	–1.677	0.92876	–1.667	0.92044	–1.657	0.90235	–1.626	0.88400	–1.612
0.5214	0.93834	–1.582	0.93059	–1.585	0.92206	–1.552	0.91798	–1.552	0.90968	–1.550	0.89157	–1.527	0.87327	–1.522
0.6594	0.92388	–1.232	0.91590	–1.238	0.90739	–1.214	0.90332	–1.220	0.89504	–1.230	0.87715	–1.232	0.85870	–1.217
0.7835	0.91402	–0.882	0.90567	–0.870	0.89687	–0.825	0.89269	–0.825	0.88442	–0.843	0.86648	–0.846	0.84807	–0.829
0.9103	0.90517	–0.414	0.89684	–0.411	0.88799	–0.362	0.88361	–0.344	0.87543	–0.376	0.85745	–0.377	0.83909	–0.356
0.9545	0.90224	–0.217	0.89396	–0.223	0.88524	–0.187	0.88102	–0.186	0.87259	–0.193	0.85467	–0.199	0.83639	–0.186
1.0000	0.89932	–	0.89097	–	0.88257	–	0.87835	–	0.86986	–	0.85189	–	0.83375	–

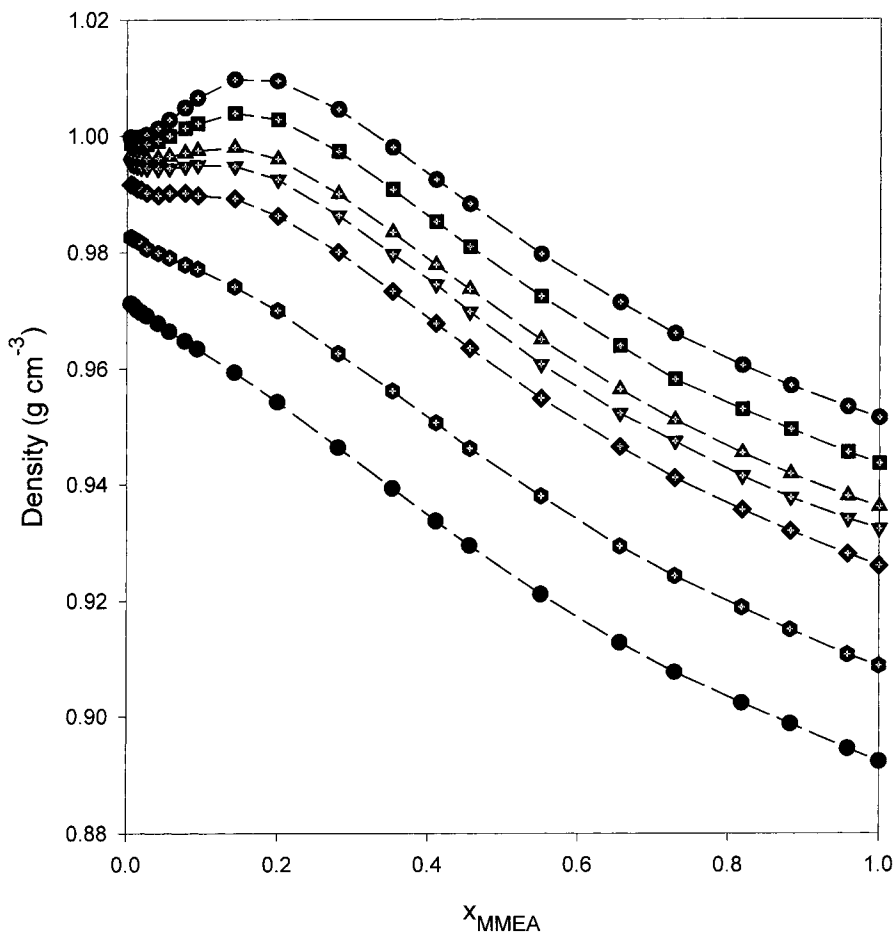


Fig. 1. Densities of (MMEA + H<sub>2</sub>O) mixtures at 5 °C (●); 15 °C (■); 25 °C (▲); 30 °C (▼); 40 °C (◆); 60 °C (○); 80 °C (○).

around 40 °C. One may speculate a “non-random distribution of water and ethanolamine molecules” or “micelle formation” at the concentration with maximum density, where the molecules of water and alkanolamines are in a more compact aggregation than other concentration zones. At the higher temperatures, there will be a competition between this molecular organization and thermal agitation. Thermal agitation is dominant at temperatures higher than 40 °C and vice versa at temperatures lower than 40 °C.

The magnitude of these maxima and minima (S-shape) at low mole fractions of ethanolamines is greater for the MMEA + H<sub>2</sub>O system than the DMEA + H<sub>2</sub>O system. This result could be related

to the way of packing of the water and alkanolamine molecules in this zone.

Excess molar volumes are calculated by [3]

$$V^E = V - x_1 V_1^* - x_2 V_2^* \quad (1)$$

where  $V$  is the volume of a mixture containing 1 mole of alkanolamine + water,  $x_1$  and  $x_2$  are the mole fractions of water and alkanolamine, respectively, and  $V_1^*$  and  $V_2^*$  are molar volumes of the pure components. Eq. (1) can be written as

$$V^E = \left[ \frac{(x_1 M_1 + x_2 M_2)}{d} \right] - \left[ \frac{x_1 M_1}{d_1^*} + \frac{x_2 M_2}{d_2^*} \right] \quad (2)$$

where  $M_1$  and  $M_2$  are the molar masses of water and alkanolamine, respectively, and  $d$ ,  $d_1^*$ ,  $d_2^*$  are the

densities of a mixture of specified mole fraction of pure water and of pure alkanolamine, respectively.

Excess molar volumes are negative for all three systems as are other (alkanolamine + H<sub>2</sub>O) mixtures [2–6]. Excess molar volumes of three (MEA + H<sub>2</sub>O, MMEA + H<sub>2</sub>O and DMEA + H<sub>2</sub>O) systems as a function of compositions at 5 °C are given in Fig. 2. The effect of the methyl group is reflected in this plot: the larger the alkyl group, the more negative is the excess molar volume.

The partial molar volume of each component ( $V_i$ ) is defined by

$$\bar{V}_i = \left( \frac{\partial V}{\partial n_i} \right)_{T,P,n_j} \quad (3)$$

One may obtain the following equations by differentiation of Eq. (1) and combination with Eq. (3):

$$\bar{V}_1 = V^E + V_1^* - x_2 \left( \frac{\partial V^E}{\partial x_2} \right)_{P,T} \quad (4)$$

and

$$\bar{V}_2 = V^E + V_2^* + (1 - x_2) \left( \frac{\partial V^E}{\partial x_2} \right)_{P,T} \quad (5)$$

where  $\bar{V}_1$  and  $\bar{V}_2$  are the partial molar volumes of water and alkanolamines, respectively.

Determination of  $V_1$  and  $V_2$  from Eqs. (4) and (5) can be obtained by using the Redlich–Kister equation:

$$V^E = x_2(1 - x_2) \sum A_n(1 - 2x_2)^n \quad (6)$$

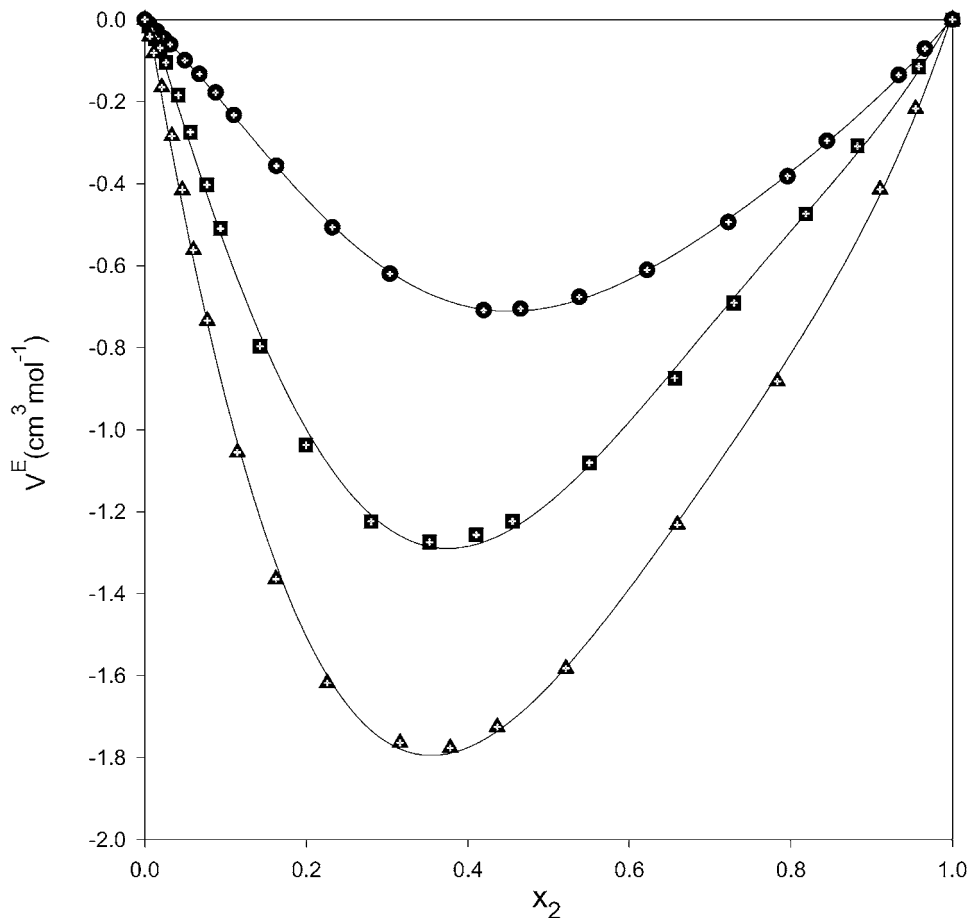


Fig. 2. Excess molar volumes of (MEA + H<sub>2</sub>O) (●); (MMEA + H<sub>2</sub>O) (■); and (DMEA + H<sub>2</sub>O) (▲) mixtures at 5 °C.

Table 4

Redlich–Kister equation fitting coefficients and the standard deviation ( $\sigma$ ) for MEA + H<sub>2</sub>O, MMEA + H<sub>2</sub>O and DMEA + H<sub>2</sub>O mixtures

$t$ (°C)	$A_0$ ( $A_6$ )	$A_1$ ( $\sigma \times 10^3$ )	$A_2$	$A_3$	$A_4$	$A_5$
MEA + H <sub>2</sub> O						
5	-2.7800 (-1.6853)	-0.8018 (1.6)	0.0411	1.5032	2.3251	-0.5744
15	-2.6536 (-1.3261)	-0.6355 (3.4)	0.1039	1.1113	2.0135	-0.2271
MMEA + H <sub>2</sub> O						
5	-4.6485 (2.1643)	-2.7645 (2.9)	-1.2096	-1.4113	0.8355	4.1634
15	-4.5773 (2.5122)	-2.7541 (3.7)	-0.7779	0.1774	-0.0976	2.3323
25	-4.4607	-2.4630 (3.7)	-1.2072	-0.1945	2.4571	2.1786
30	-4.3793	-2.3969 (3.8)	-1.2333	-0.4256	2.7165	2.0547
40	-4.3476	-2.1323 (4.3)	-1.3081	-0.5644	2.4405	2.4652
60	-4.2321	-1.7812 (4.1)	-1.0648	0.4788	1.7697	0.6514
80	-4.1365	-1.6721 (4.3)	-0.7571	0.4616	0.9249	0.6040
	$A_1$ ( $A_7$ )	$A_2$ ( $\sigma \times 10^3$ )				
DMEA + H <sub>2</sub> O						
5	-6.5137 (8.9452)	-4.0922 (10.636)	-1.0387 (3.2)	3.7547	-7.1556	-10.885
15	-6.5116 (7.7319)	-3.7784 (10.626)	-0.3293 (3.5)	3.5580	-6.9114	-10.776
25	-6.3801 (5.8052)	-3.6514 (8.6773)	-0.4034 (3.8)	2.9202	-4.7396	-9.1581
30	-6.3477 (2.4245)	-3.4446 (9.8235)	-1.1476 (2.1)	2.6534	-1.0594	-10.080
40	-6.3536 (4.4341)	-3.2659 (5.8293)	-0.3820 (4.1)	2.1908	-3.7632	-6.3708
60	-6.2503 (1.3398)	-2.9976 (5.5774)	-0.9885 (3.4)	2.1166	-0.7648	-6.3726
80	-6.2191 (2.1746)	-2.3804	0.0103 (4.4)	-1.5579	-2.4108	1.5428

Redlich–Kister coefficients ( $A_n$ ) and the standard deviation ( $\sigma$ ) for these mixtures are given in Table 4 for MEA + H<sub>2</sub>O, MMEA + H<sub>2</sub>O and DMEA + H<sub>2</sub>O mixtures. They were obtained by fitting the data using a least squares program. All the fitted polynomials were examined by the  $F$ -test [14,15]. This is a test of goodness of fitting of the power of a polynomial.

Differentiation of Eq. (6) with respect to  $x_2$  and substitution of the result in Eqs. (4) and (5) leads to the following equations for the partial molar volumes of water  $\bar{V}_1$  and alkanolamine  $\bar{V}_2$ :

$$\bar{V}_1 = V_1^* + x_2^2 \sum A_n (1 - 2x_2)^n + 2x_2^2 (1 - x_2) \sum n A_n (1 - 2x_2)^{n-1} \quad (7)$$

and

$$\bar{V}_2 = V_2^* + (1 - x_2)^2 \sum A_n (1 - 2x_2)^n - 2x_2 (1 - x_2)^2 \sum n A_n (1 - 2x_2)^{n-1} \quad (8)$$

Much of our interest in the volumetric properties of (water + alkanolamine) systems is focussed on the partial molar volumes of the alkanolamines at infinite dilution ( $x_2 = 0$ ) in water and of water in alkanolamines

at infinite dilution ( $x_1 = 0$ ). By setting  $x_2 = 1$  (corresponding to  $x_1 = 0$ ) in Eq. (7) will lead to

$$\bar{V}_1^\infty = V_1^* + \sum A_n (-1)^n \quad (9)$$

Similarly, setting  $x_2 = 0$  in Eq. (8) will lead to

$$\bar{V}_2^\infty = V_2^* + \sum A_n \quad (10)$$

Table 5

Partial molar volumes (cm<sup>3</sup>/mol) of alkanolamines at infinite dilution in water

$t$ (°C)	MEA <sup>a</sup>	MMEA	DMEA
5	57.4	76.1	92.8
15	58.3	76.4	93.7
20	–	–	93.6 <sup>b</sup>
25	59.2	76.5	94.1
			93.9 <sup>b</sup>
30	59.4	76.9	94.3
			94.2 <sup>b</sup>
40	59.7	77.7	94.8
			94.9 <sup>b</sup>
60	60.5	78.5	96.3
80	61.4	79.6	98.1

<sup>a</sup> MEA values from 25 to 80 °C are from [4].

<sup>b</sup> Calculated by using the Redlich–Kister coefficients given in [6].

In Eqs. (9) and (10),  $\bar{V}_1^\infty$  and  $\bar{V}_2^\infty$  represent the partial molar volumes of water at infinite dilution in alkanolamine and the partial molar volume of alkanolamine at infinite dilution in water, respectively. Eqs. (7) and (8) allow the calculation of the partial molar volumes of each component over the whole range of concentration. The values of  $\bar{V}_2^\infty$  for MMEA and DMEA are given in Table 5 ( $\bar{V}_1^\infty$  values are practically constant for the measured temperatures). Our values are in excellent agreement with the values from [6], using Eqs. (9) and (10). The composition dependence of the partial molar volume for DMEA in (DMEA + H<sub>2</sub>O) mixtures is shown in Fig. 3. This plot shows a minimum value for  $\bar{V}_2$  around  $x_2 = 0.12$  at lower

temperature (5 °C), which disappears with increase of the temperature. This is consistent with all the other (water + polar organic compounds) mixtures [4,9–14].

As shown previously [3,4], the apparent molar volume of water ( $V_{\phi,1}$ ) and the apparent molar volume of alkanolamine in water ( $V_{\phi,2}$ ) can be calculated as

$$V_{\phi,1} = V_1^* + \left(\frac{V^E}{x_1}\right) = V_1^* + \left[\frac{V^E}{1-x_2}\right] \quad (11)$$

and

$$V_{\phi,2} = V_2^* + \left(\frac{V^E}{x_2}\right) \quad (12)$$

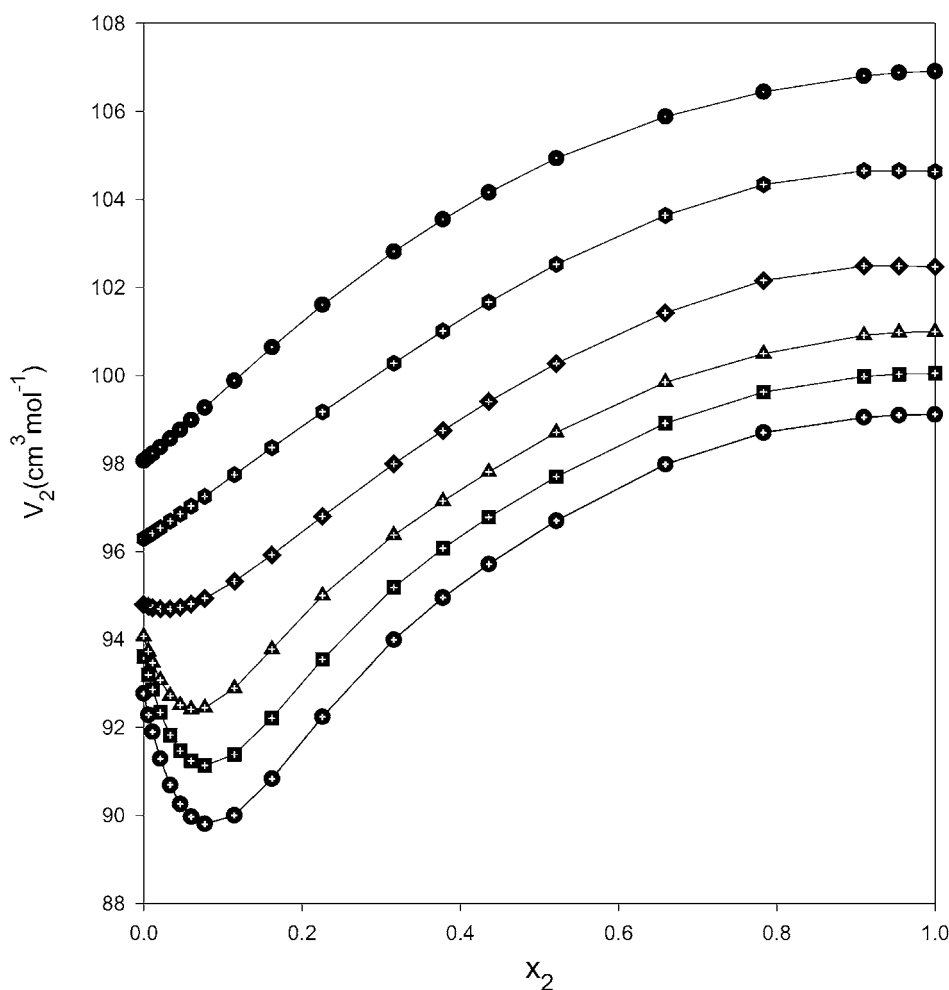


Fig. 3. Partial molar volumes of DMEA in (DMEA + H<sub>2</sub>O) mixtures at 5 °C (●); 15 °C (■); 25 °C (▲); 40 °C (◆); 60 °C (○); and 80 °C (○).

Simple graphical extrapolation of  $V_{\phi,1}$  to  $x_1 = 0$  or ( $x_2 = 1$ ) leads to the desired value of  $\bar{V}_1^\infty$  and similar extrapolation of  $V_{\phi,2}$  to  $x_2 = 0$  leads to the desired value of  $\bar{V}_2^\infty$ .

Another method to obtain the partial molar quantities from the excess molar quantities was developed by Perron et al. [16]. This technique consists of a linear extrapolation of reduced excess molar volume ( $V^E/x_1x_2$ ), to  $x_2 = 0$  (or  $x_1 = 1$ ). The extrapolated values of reduced excess molar volume at  $x_1 = 0$  or  $x_2 = 0$  will give  $\bar{V}_1^\infty$  and  $\bar{V}_2^\infty$ , respectively. The largest disagreement between  $\bar{V}_2^\infty$  values calculated by these three ways is  $0.3 \text{ cm}^3/\text{mol}$ .

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