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Volumetric properties of aqueous solutions of mono, and diethylethanolamines at temperatures from 5 to 80 °C II

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Abstract

Densities of aqueous solutions of monoethylethanolamine (MEEA) and diethylethanolamine (DEEA) were measured over the whole range of concentrations at temperatures from 5 to 80 °C. Densities of these systems show different behavior at both lower and higher concentration of ethanolamine. This behavior was classified into two zones: at $x_2 = 0.12$ for (MEEA + water) and at $x_2 = 0.04$ for (DEEA + water) mixtures. It is found that in the low concentration zone the effect of alkyl groups could be shown as:

$$-CH_3 > -C_2H_5 > 2(-CH_3) > 2(-C_2H_5)$$

The excess molar volumes and excess molar enthalpies of (alkylethanolamine + water) mixtures show similar dependence on the size of the alkyl group present in the alkyethanolamines. The excess molar volumes have the most negative value for the (ethylethanolamine + water) system, while the excess molar enthalpies of the (MEEA + water) system have the more negative value.

Keywords: Binary aqueous systems; Monoethylethanolamine; Diethylethanolamine; Density; Excess molar volume; Partial molar volume; Excess molar enthalpy

1. Introduction

This is second part of the preceding paper [1] on the densities and volumetric properties of aqueous solutions of methyl and ethyl derivatives of ethanolamine. In this paper, we report the densities and excess molar volumes of (MEEA + water) and (DEEA + water) mixtures at temperatures from 5 to 80 °C.

2. Experimental

MEEA [$C_2H_5HNC_2H_4OH$, MEEA (99%)] and DEEA [$(C_2H_5)_2$ NC_2H_4OH, DEEA (>99%)] were obtained from Fluka Chemical. These compounds were used as received, after confirmatory analysis by titration with standard hydrochloric acid. Mixtures of these alkanolamines with nano-pure distilled water were made by weighing (an accuracy of 1×10^{-4}) with care being taken to minimize exposure to air (carbon dioxide). The details of measurements have been given earlier [3,4].

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Table 1
Compositions, densities (g cm^{-3}), and excess molar volumes (cm^3 mol^{-1}) for MEEA (2) + H_2O (1) mixtures

x_{MEEA}	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	0.000	0.99910	0.000	0.99704	0.000	0.99565	0.000	0.99222	0.000	0.98320	0.000	0.97180	0.000
0.0061	0.99938	−0.031	0.99835	−0.033	0.99613	−0.033	0.99465	−0.034	0.99114	−0.035	0.98179	−0.035	0.97033	−0.038
0.0100	0.99914	−0.054	0.99802	−0.056	0.99563	−0.060	0.99415	−0.057	0.99052	−0.059	0.98096	−0.058	0.96948	−0.064
0.0217	0.99897	−0.130	0.99744	−0.133	0.99464	−0.132	0.99299	−0.133	0.98906	−0.134	0.97889	−0.133	0.96692	−0.137
0.0333	0.99947	−0.220	0.99728	−0.217	0.99414	−0.215	0.99225	−0.215	0.98782	−0.211	0.97707	−0.208	0.96452	−0.208
0.0467	1.00038	−0.331	0.99752	−0.322	0.99381	−0.316	0.99162	−0.313	0.98674	−0.305	0.97517	−0.295	0.96196	−0.289
0.0622	1.00141	−0.462	0.99794	−0.448	0.99348	−0.433	0.99092	−0.425	0.98554	−0.413	0.97293	−0.391	0.95907	−0.378
0.0772	1.00262	−0.595	0.99819	−0.568	0.99298	−0.541	0.99017	−0.530	0.98418	−0.509	0.97078	−0.478	0.95626	−0.456
0.1167	1.00278	−0.879	0.99669	−0.827	0.99033	−0.784	0.98694	−0.766	0.97996	−0.730	0.96492	−0.678	0.94917	−0.638
0.1656	0.99889	−1.111	0.99189	−1.047	0.98496	−1.002	0.98123	−0.978	0.97359	−0.932	0.95758	−0.871	0.94103	−0.819
0.2308	0.99102	−1.282	0.98378	−1.224	0.97660	−1.182	0.97264	−1.157	0.96476	−1.112	0.94825	−1.053	0.93117	−0.993
0.3169	0.98021	−1.369	0.97288	−1.324	0.96562	−1.292	0.96175	−1.277	0.95381	−1.237	0.93702	−1.185	0.91978	−1.126
0.3893	0.97177	−1.360	0.96439	−1.324	0.95731	−1.310	0.95336	−1.296	0.94542	−1.262	0.92860	−1.219	0.91146	−1.170
0.4490	0.96559	−1.320	0.95822	−1.293	0.95098	−1.279	0.94703	−1.267	0.93911	−1.238	0.92245	−1.213	0.90524	−1.161
0.5356	0.95729	−1.194	0.94992	−1.179	0.94269	−1.176	0.93883	−1.174	0.93103	−1.157	0.91420	−1.131	0.89718	−1.091
0.6845	0.94547	−0.878	0.93803	−0.876	0.93073	−0.883	0.92680	−0.882	0.91917	−0.886	0.90238	−0.874	0.88547	−0.839
0.8213	0.93688	−0.520	0.92928	−0.519	0.92191	−0.531	0.91798	−0.535	0.91033	−0.543	0.89351	−0.536	0.87671	−0.506
0.9202	0.93181	−0.244	0.92414	−0.245	0.91661	−0.249	0.91268	−0.255	0.90495	−0.261	0.88812	−0.255	0.87149	−0.239
0.9560	0.93009	−0.134	0.92243	−0.139	0.91488	−0.137	0.91089	−0.146	0.90312	−0.146	0.88629	−0.141	0.86975	−0.134
1.0000	0.92813	0.000	0.92039	0.000	0.91278	0.000	0.90877	0.000	0.90097	0.000	0.88418	0.000	0.86772	0.000

Table 2
Compositions, densities (g cm^{-3}), and excess molar volumes (cm^3 mol^{-1}) for DEEA (2) + H_2O (1) mixtures

x_{DEEA}	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	0.000	0.99910	0.000	0.99704	0.000	0.99565	0.000	0.99222	0.000	0.98320	0.000	0.97180	0.000
0.0039	0.99914	−0.037	0.99835	−0.043	0.99605	−0.043	0.99465	−0.045	0.99114	−0.048	0.98196	−0.051	0.97025	−0.052
0.0080	0.99855	−0.081	0.99769	−0.091	0.99522	−0.091	0.99349	−0.089	0.98989	−0.094	0.98038	−0.099	0.96865	−0.106
0.0121	0.99831	−0.130	0.99711	−0.139	0.99447	−0.141	0.99283	−0.142	0.98898	−0.147	0.97897	−0.148	0.96692	−0.155
0.0169	0.99814	−0.191	0.99687	−0.203	0.99381	−0.202	0.99192	−0.201	0.98782	−0.205	0.97765	−0.212	0.96493	−0.212
0.0261	0.99814	−0.312	0.99568	−0.311	0.99257	−0.318	0.99059	−0.320	0.98592	−0.321	0.97459	−0.317	0.96126	−0.318
0.0372	0.99855	−0.468	0.99478	−0.450	0.99108	−0.455	0.98860	−0.451	0.98327	−0.447	0.97095	−0.438	0.95660	−0.429
0.0602	0.99748	−0.747	0.99173	−0.703	0.98702	−0.703	0.98380	−0.691	0.97739	−0.679	0.96286	−0.644	0.94705	−0.624
0.0909	0.99317	−1.033	0.98508	−0.946	0.98015	−0.964	0.97644	−0.947	0.96897	−0.925	0.95297	−0.878	0.93578	−0.845
0.1326	0.98548	−1.319	0.97642	−1.217	0.97090	−1.246	0.96677	−1.225	0.95850	−1.198	0.94125	−1.140	0.92209	−1.065
0.1883	0.97503	−1.585	0.96675	−1.528	0.95962	−1.529	0.95509	−1.503	0.94650	−1.484	0.92817	−1.412	0.90788	−1.310
0.2629	0.96297	−1.829	0.95493	−1.808	0.94684	−1.794	0.94245	−1.783	0.93308	−1.749	0.91322	−1.625	0.89276	−1.524
0.3136	0.95557	−1.920	0.94738	−1.908	0.93909	−1.896	0.93459	−1.886	0.92521	−1.860	0.90488	−1.713	0.88436	−1.611
0.3789	0.94687	−1.959	0.93844	−1.951	0.92975	−1.929	0.92519	−1.921	0.91533	−1.873	0.89546	−1.754	0.87499	−1.655
0.4547	0.93795	−1.920	0.92882	−1.878	0.92007	−1.862	0.91511	−1.829	0.90512	−1.775	0.88615	−1.723	0.86590	−1.640
0.5883	0.92455	−1.654	0.91538	−1.623	0.90625	−1.587	0.90136	−1.561	0.89166	−1.536	0.87272	−1.493	0.85234	−1.385
0.6638	0.91795	−1.402	0.90884	−1.384	0.89978	−1.358	0.89499	−1.343	0.88528	−1.319	0.86653	−1.296	0.84623	−1.185
0.7858	0.90905	−0.933	0.90015	−0.948	0.89166	−0.996	0.88689	−0.985	0.87700	−0.941	0.85795	−0.880	0.83816	−0.817
0.8765	0.90361	−0.553	0.89455	−0.557	0.88609	−0.617	0.88123	−0.595	0.87150	−0.670	0.85262	−0.526	0.83321	−0.509
0.9544	0.89956	−0.212	0.89039	−0.205	0.88172	−0.243	0.87696	−0.234	0.86735	−0.225	0.84864	−0.202	0.82936	−0.200
1.0000	0.89737	0.000	0.88823	0.000	0.87929	0.000	0.87459	0.000	0.86504	0.000	0.84649	0.000	0.82724	0.000

3. Results

The densities and excess molar volumes of (MEEA + H_2O) and (DEEA + H_2O) mixtures are given in Tables 1 and 2, respectively. The composition dependence of these two binary mixtures are similar to the aqueous solutions of MEEA and DEEA systems [1], but are different from other (ethanolamine + water) systems [2,3,4]. The density behavior of these two binary systems was divided in two zones of mole fractions of alkanolamines [1]. This separation line occurs at $x_2 = 0.12$ for (MEEA + H_2O) and $x_2 = 0.04$ for (DEEA + H_2O) mixtures.

The composition dependence of the densities of the aqueous solutions of MEA, MMEA, DMEA, MEEA and DEEA in the low concentration zone of alkanolamines at 5 °C is shown in Fig. 1. The density of aqueous solutions of MEA (without any methyl or ethyl group) varies in a monotonic fashion in this range of concentration (with a maximum at $x_2 = 0.425$). The densities of the other four aqueous solutions show an S-shape where the density values pass through a minimum and then a maximum at increasing alkylethanolamine concentration. This S-shape is much more pronounced for MMEA and it becomes much smaller by replacing the methyl group by an ethyl group and by also adding a second methyl and ethyl group (dialkyl derivatives). We could not extend our studies to the larger alkyl groups due to their immiscibilities in water (*n*-propylethanolamine

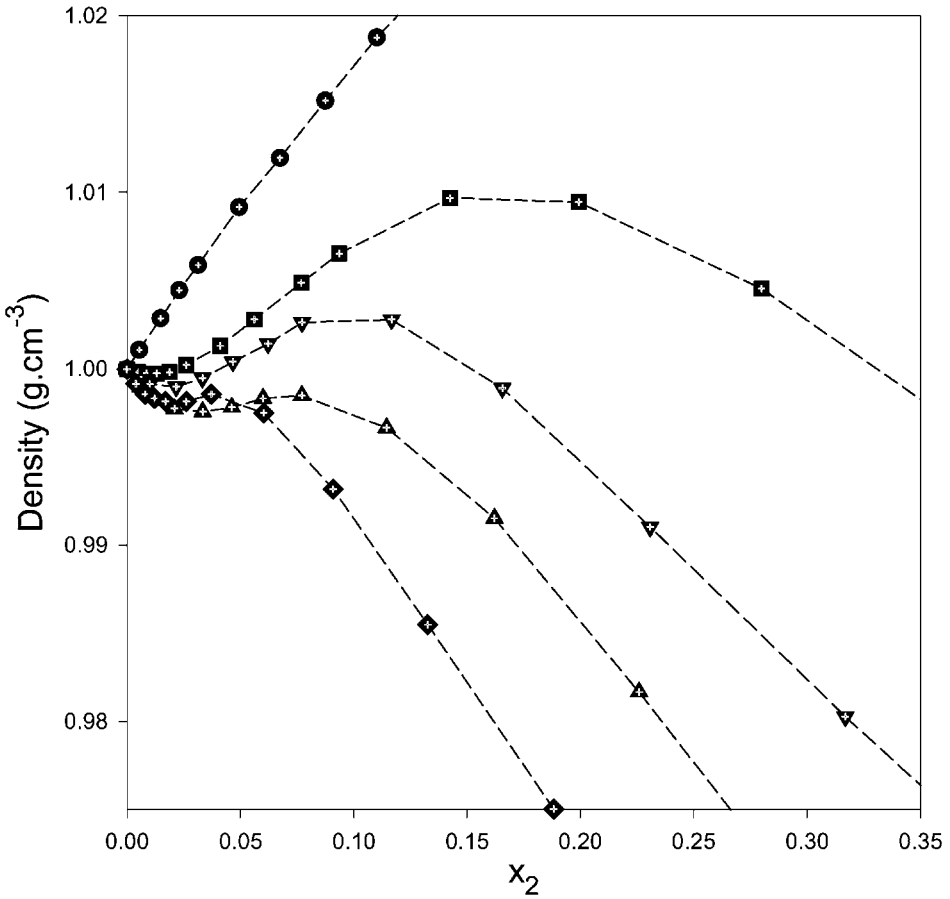

Fig. 1. Composition dependence of the density of aqueous solutions of alkanolamines at low mole fraction of alkanolamine at 5 °C: ●, (MEA + H_2O); ■, (MMEA + H_2O); ▽, (DMEA + H_2O); ▲, (MEEA + H_2O); ◆, (DEEA + H_2O).

is immiscible at $0.04 < x_2 < 0.12$) [11]. The effect of an additional $-C_2H_4OH$ group on the nitrogen atom makes these compounds more soluble in water; *n*-butyldiethanolamine with a much bigger alkyl group is completely miscible with water. This kind of density behavior at lower mole fractions of ethanolamines also has been seen for (2-amino-2-methyl-1-propanol + H_2O) mixtures [11].

The excess molar volumes of the (MEEA + H_2O) and (DEEA + R_2O) mixtures have been determined as in [1] and are given in Tables 1 and 2 respectively. In both cases, the excess molar volumes are negative as in all the other (ethanolamines + H_2O) mixtures [2,3,4]. The composition dependence of the excess molar volume of (MEA + H_2O), (MMEA + H_2O), (DMEA+H_2O), (MEEA+H_2O) and (DEEA+ H_2O) mixtures at 5 °C is shown in Fig. 2. This plot shows that the position of the minimum becomes more negative by adding more methyl or ethyl groups to the nitrogen atom of alkanolamine. The size effect of alkyl groups on the excess molar volume of these aqueous solutions of alkylethanolamines could be also presented by reduced excess molar volume [7]. The reduced excess molar volumes of (MEA + H_2O), (MMEA + H_2O), (DMEA + H_2O), (MEEA + H_2O) and (DEEA + H_2O) mixtures against the mole fraction of ethanolamine at 5 °C are plotted in Fig. 3. Here in this plot, the bigger the alkyl group on the ethanolamine, the more negative is the minimum of reduced excess molar volume. One more significant effect is the position of minimum, for the alkylethanolamine with a bigger alkyl group the minimum is much to the lower concentration of alkylethanolamine. This means that for the formation of the

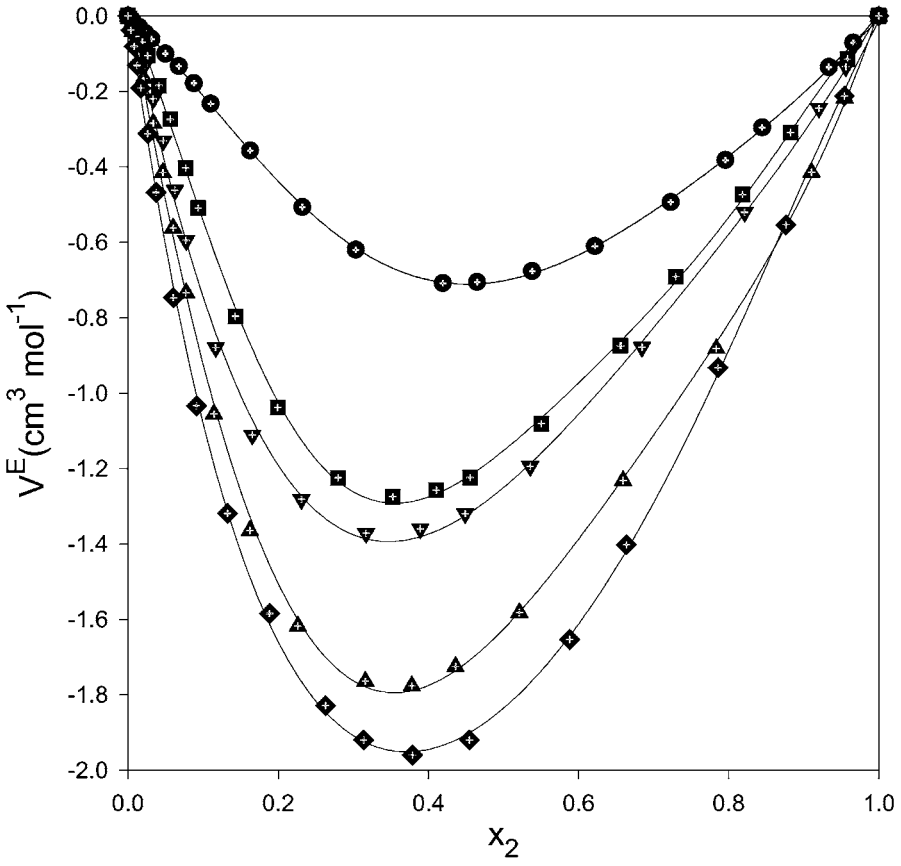

Fig. 2. Excess molar volumes of ●, (MEA + H_2O); ■, (MMEA + R_2O), ▲, (DMEA + H_2O); ▼, (MEEA + H_2O); ◆, (DEEA + H_2O) mixtures at 5 °C.

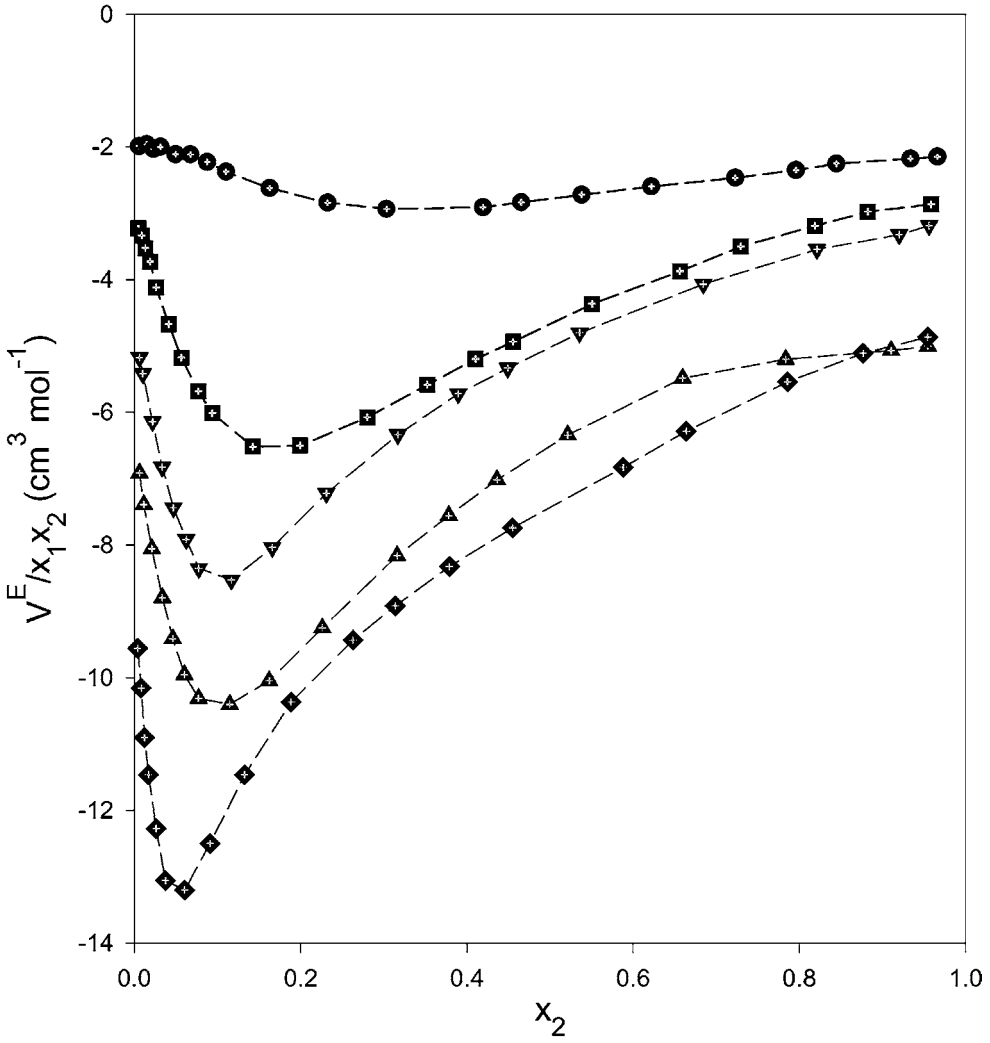

Fig. 3. Reduced excess molar volumes of ●, (MEA + H_2O); ■, (MMEA + H_2O); ▲, (DMEA + H_2O); ▼, (MEEA + H_2O) and ◆, (DEEA + H_2O) mixtures at 25 °C.

aggregates between alkylethanolamine and water, a larger number of water molecules are needed. The reduced excess molar volumes of mono and dialkyl (methyl, and ethyl) are well separated from each other.

The comparable effect has been reported for the excess molar enthalpies for these systems [6,8,9]. The effect of alkyl groups on the position of the minimum of the excess molar volumes and the excess molar enthalpies of aqueous solutions of mono and dialkylethanolamines is shown in Fig. 4. The behavior of the excess molar volumes and excess molar enthalpies is practically the same function of the number of the carbon atoms on the alkyl groups. In both cases, the excess molar volumes and excess molar enthalpies are more negative for dialkylethanolamines than monoalkylethanolamines. The excess molar volume shows a minimum value for ethylethanolamine, while for the excess molar enthalpies the minimum value is for methylethanolamines. This similar behavior suggests that there is some relation between these two excess properties, both reflecting the molecular

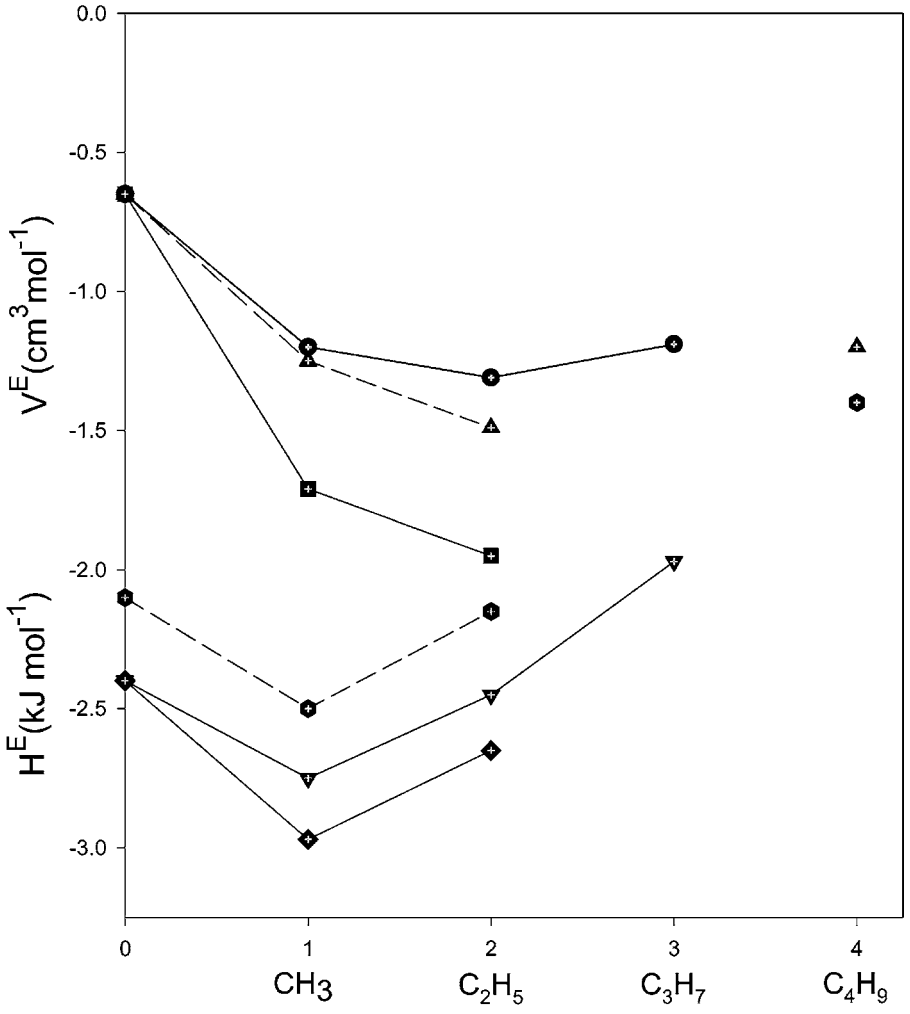

Fig. 4. Variation of the minima of the excess molar volume (V^E) and excess molar enthalpy (H^E) with the size of alkyl groups (methyl, ethyl, and *n*-propyl and *n*-butyl) for: (a) V^E ● (MEEA + H_2O); ■ (DEEA + H_2O) and ▲, (alkyldiethnolamines + H_2O); (b)H^E ▼, (MEEA + H_2O); ◆, (DEEA + H_2O) and ●, (alkyldiethnolamines + H_2O) mixture.

interactions between water and alkylethanolamine molecules.

The temperature effect on the excess molar volumes is the same for all the (alkylethanolamine + H_2O) mixtures: the higher the temperature, the less negative the excess molar volume. The excess molar volume of the (MEEA + H_2O) system at temperatures from 5 to 80 °C is shown in Fig. 5.

The Redlich–Kister equation coefficients and the standard deviation (σ) for (MMEA + H_2O) and (DEEA + H_2O) mixtures are given in Table 3. These coefficients were obtained by fitting the data using a least squares program. All the fitted polynomials were examined by the *F*-test [8–10]. This is a test of the goodness of fit of the power of the polynomial. By comparing the aqueous solutions of MEA, MMEA and DMEA [1] and the aqueous solutions of MEEA and DEEA from this paper, one may observe that the bigger the size and the higher the number of alkyl group, the higher the degree of fitted polynomial. The values of $\overline{V}_2^{\infty}$ for MEEA and DEEA, calculated in the same way as in [1], are given in Table 4.

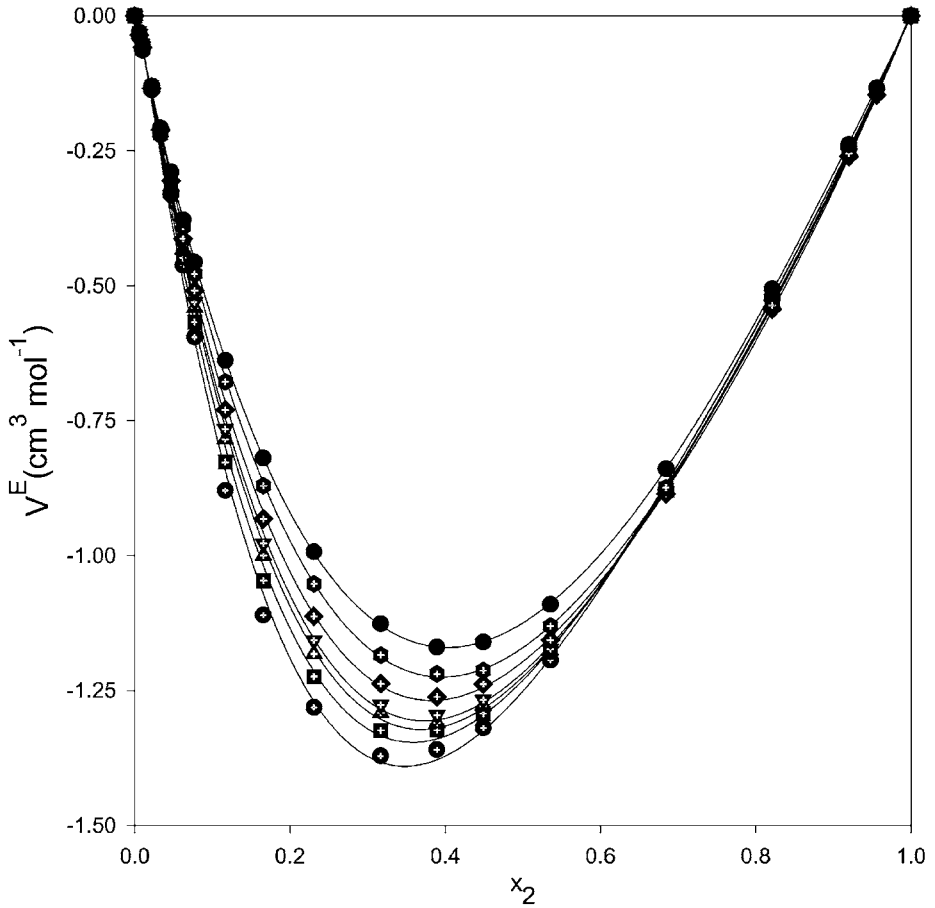

Fig. 5. Excess molar volume of (MEEA + H_2O) mixtures at various temperature ●, 5 °C; ■, 15 °C; ▲, 25 °C; ▼, 30 °C; ◆, 40 °C; ⬢, 60 °C; and ●, 80 °C.

Table 3
Redlich–Kister equation fitting coefficients and the S.D. (σ) for (MEEA + H_2O) and (DEEA + H_2O) mixtures at several temperatures

t (°C)	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	$\sigma \times 10^3$
MEEA + H_2O												
5	−5.0412	−2.8601	0.0398	−1.2026	8.1451	−2.8560	9.3290	6.1742				5.2
15	−4.9538	−2.7085	−0.0536	−0.0052	−6.0939	−4.9663	6.8789	6.9786				4.1
25	−4.9276	−2.6307	0.1262	1.1960	−5.7503	−6.2606	6.3599	6.8009				3.6
30	−4.8972	−2.5626	0.1100	1.6189	−5.0430	−6.9414	5.3803	7.1157				3.6
40	−4.8084	−2.2608	−0.0742	1.1914	−3.8861	−5.2822	4.1807	5.3984				3.6
60	−4.7023	−2.1938	0.1895	2.7498	−3.3431	−7.9591	3.2789	6.3830				4.5
80	−4.5012	−1.5270	−0.4725	−1.6634	0.0996	1.6452	–	–				4.7
DEEA + H_2O												
5	−7.4590	−3.3913	1.4257	−3.7072	−24.221	13.616	92.646	−27.797	−153.67	17.752	86.122	2.6
15	−7.2885	−3.3722	−0.5034	−6.4185	−13.431	33.810	61.984	−60.289	−101.79	32.835	53.833	5.2
25	−7.2067	−3.8290	0.8379	−0.5924	−27.396	15.708	95.728	−36.413	−137.73	21.972	68.283	4.4
30	−7.0576	−3.8414	−1.4466	−2.3124	−10.656	28.998	45.743	−64.358	−69.013	39.358	33.641	4.9
40	−6.8577	3.3895	−3.1915	−7.2318	4.3767	43.911	−0.8270	−81.944	−6.7514	46.520	3.570	4.9
60	−6.6948	−2.9736	−0.5532	−0.3606	−1.5511	−0.9633	5.1					
80	−6.3112	−3.3687	0.2753	2.4778	−2.9673	−3.7297	4.8					

Table 4
Partial molar volumes ($cm^3\,mol^{-1}$) of alkanolamines at infinite dilution in water

t (°C)	MEEA	DEEA
5	91.5	121.7
15	91.9	121.3
20		122.1[a]
25	92.7	122.6
		122.7[a]
30	92.9	123.0
		122.7[a]
40	93.4	123.7
		123.6[a]
60	95.2	125.3
80	96.3	128.0

[a] Calculated from the Redlich–Kister coefficients given in [5].

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