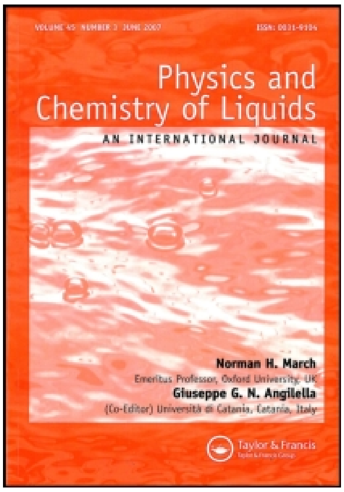

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Densities and excess molar volumes of aqueous solutions of some diethanolamines

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Densities and excess molar volumes of aqueous solutions of some diethanolamines

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Densities of aqueous diethanolamine (DEA), methyldiethanolamine (MDEA), ethyldiethanolamine (EDEA) and *n*-butyldiethanolamine (BDEA) solutions were determined from 303.15 to 323.15 K at different compositions in the range $0 \leq x_1 \leq 1$, where x_1 is the mole fraction of alkanolamines. The densities of the diethanolamines are assumed to be related to the strength of association. Excess molar volumes have been calculated from the density data. The V_m^E values have been found to be negative for all systems in the whole range of composition at all temperatures, and less negative with increasing temperature. Negative values of V_m^E can be explained by the large difference in the molar volumes. For all systems, minima occur at about 0.35–0.40 mole fraction of diethanolamines. The depth of minima varies as $\text{EDEA} + \text{W} > \text{MDEA} + \text{W} > \text{BDEA} + \text{W} > \text{DEA} + \text{W}$. All the data have been correlated with six-degree polynomial equations.

Keywords: densities; excess molar volumes; strength of association; molar volumes; hydrophobicity; diethanolamines

1. Introduction

As part of an ongoing programme on studies of molecular interactions in aqueous organic mixtures, we have published some papers [1–15] which include amines, nitriles, sulfolanes, alkylcarbonates, alcohols, sulfoxides, furans, formamides, etc. However, we have missed studying the physicochemical properties of aqueous solutions of alkanolamines, which are very important in terms of scientific interest as well as for industrial purposes. A recent literature survey shows that quite a large number of investigations have been conducted on volumetric and viscometric properties of binary aqueous and non-aqueous systems comprising of different alkanolamines.

Among these, Alvarez *et al.* [16] measured the density and speed of sound of ethanol + methyldiethanolamine (MDEA) and ethanol + triethanolamine (TEA) solutions; Galicia-Luna *et al.* [17] studied the densities of an aqueous solution of MDEA; Iglesias-Silva and co-workers [18,19] measured the densities of an aqueous solution of MDEA and also the densities and viscosities of *N*,*N*-dimethylethanolamine (DMEA) + water; and Fischer *et al.* [20] also reported the densities of the aqueous solutions of DEA, MDEA and *n*-butylethanolamine (BEA). In a series of works, Mather *et al.* [21–25] reported on the densities of water + 2-amino-2-methyl-1-propanol (AMP), + *n*-butyldiethanolamine

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Table 1. Experimental and literature densities of pure DEA, MDEA, EDEA and BDEA at different temperatures.

Sample	T (K)	Density, ρ (g cm^{-3})	
		This work	Literature
DEA	303.15	1.09068	1.090788[a]
	308.15	1.08732	1.087508[a]
	313.15	1.08405	1.084199[a], 1.0847[b], 1.0846[c], 1.08401[d]
	318.15	1.08065	1.080862[a]
	323.15	1.07734	1.077491[a], 1.0774[b], 1.0781[c], 1077.32[d]
MDEA	303.15	1.03294	1.033056[a]
	308.15	1.02893	1.029261[a]
	313.15	1.02494	1.025447[a], 1.0250[b], 1.0247[c], 1.02445[e], 1.0272[f], 1.02519[g]
	318.15	1.02113	1.021622[a]
	323.15	1.01727	1.017781[a], 1.0174[b], 1.0173[c], 1.01699[g]
EDEA	303.15	1.00647	1.00611[e]
	308.15	1.00258	
	313.15	0.99858	0.99827[e]
	318.15	0.99461	
	323.15	0.99067	
BDEA	303.15	0.96267	0.96245[h]
	308.15	0.95879	
	313.15	0.95494	0.95518[h]
	318.15	0.95112	
	323.15	0.94733	

Note: [a]Alvarez *et al.* [38]; [b]Rebolledo-Libreros and Trejo [39]; [c]DiGuilio *et al.* [31]; [d]Mather *et al.* [24]; [e]Hepler *et al.* [27]; [f]Paul and Mandal [40]; [g]Henni *et al.* [41]; [h]Mather *et al.* [21].

Table 2. Experimental densities ρ (g cm^{-3}) and excess molar volumes V_m^E (cm^3 mol^{-1}) of the system DEA (x_1) + water (x_2) for different molar ratios at different temperatures.

T(K)	303.15		308.15		313.15		318.15		323.15	
x_1	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
0.0000	0.99567	0.0000	0.99406	0.0000	0.99224	0.0000	0.99025	0.0000	0.98807	0.0000
0.0501	1.02266	−0.1325	1.02060	−0.1311	1.01840	−0.1299	1.01607	−0.1294	1.01360	−0.1289
0.1004	1.04239	−0.2814	1.03984	−0.2747	1.03730	−0.2708	1.03470	−0.2695	1.03189	−0.2651
0.1509	1.05615	−0.4044	1.05341	−0.3975	1.05061	−0.3908	1.04774	−0.3868	1.04482	−0.3828
0.2006	1.06578	−0.4998	1.06271	−0.4870	1.05967	−0.4761	1.05664	−0.4704	1.05363	−0.4665
0.3008	1.07760	−0.6100	1.07434	−0.5958	1.07119	−0.5855	1.06797	−0.5785	1.06478	−0.5722
0.4014	1.08324	−0.6102	1.07998	−0.5995	1.07681	−0.5922	1.07359	−0.5888	1.07039	−0.5851
0.5011	1.08628	−0.5577	1.08301	−0.5497	1.07975	−0.5406	1.07651	−0.5398	1.07329	−0.5377
0.5957	1.08807	−0.4837	1.08471	−0.4741	1.08145	−0.4671	1.07814	−0.4647	1.07492	−0.4648
0.6968	1.08931	−0.3875	1.08595	−0.3804	1.08262	−0.3702	1.07930	−0.3703	1.07600	−0.3672
0.8034	1.09015	−0.2705	1.08669	−0.2590	1.08342	−0.2550	1.08001	−0.2507	1.07677	−0.2538
0.9012	1.09034	−0.1283	1.08690	−0.1196	1.08364	−0.1184	1.08040	−0.1296	1.07702	−0.1229
1.0000	1.09068	0.0000	1.08732	0.0000	1.08405	0.0000	1.08065	0.0000	1.07734	0.0000

Table 3. Experimental densities ρ (g cm^{-3}) and excess molar volumes V_m^E (cm^3 mol^{-1}) of the system MDEA (x_1) + water (x_2) for different molar ratios at different temperatures.

T(K)	303.15		308.15		313.15		318.15		323.15	
x_1	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
0.0000	0.99567	0.0000	0.99406	0.0000	0.99224	0.0000	0.99025	0.0000	0.98807	0.0000
0.0501	1.01841	−0.3014	1.01591	−0.2960	1.01342	−0.2943	1.01095	−0.2951	1.00805	−0.2897
0.1000	1.03343	−0.6006	1.03044	−0.5930	1.02748	−0.5893	1.02453	−0.5867	1.02160	−0.5884
0.1501	1.04167	−0.8244	1.03822	−0.8109	1.03480	−0.8011	1.03140	−0.7915	1.02787	−0.7815
0.1992	1.04626	−0.9933	1.04266	−0.9804	1.03900	−0.9679	1.03530	−0.9523	1.03155	−0.9386
0.2459	1.04849	−1.1083	1.04472	−1.0933	1.04091	−1.0790	1.03704	−1.0594	1.03314	−1.0424
0.2961	1.04892	−1.1671	1.04501	−1.1498	1.04120	−1.1387	1.03734	−1.1214	1.03344	−1.1063
0.3981	1.04784	−1.1954	1.04392	−1.1832	1.04004	−1.1744	1.03618	−1.1603	1.03235	−1.1520
0.5001	1.04547	−1.1224	1.04140	−1.1054	1.03752	−1.1012	1.03351	−1.0798	1.02961	−1.0699
0.5938	1.04236	−0.9483	1.03847	−0.9468	1.03461	−0.9476	1.03078	−0.9396	1.02698	−0.9385
0.7022	1.03946	−0.7352	1.03549	−0.7312	1.03163	−0.7359	1.02786	−0.7348	1.02398	−0.7295
0.7945	1.03719	−0.5244	1.03316	−0.5177	1.02931	−0.5266	1.02541	−0.5152	1.02162	−0.5193
0.9015	1.03481	−0.2551	1.03086	−0.2593	1.02694	−0.2650	1.02313	−0.2633	1.01934	−0.2700
1.0000	1.03294	0.0000	1.02893	0.0000	1.02494	0.0000	1.02113	0.0000	1.01727	0.0000

Table 4. Experimental densities ρ (g cm^{-3}) and excess molar volumes V_m^E (cm^3 mol^{-1}) of the system EDEA (x_1) + water (x_2) for different molar ratios at different temperatures.

T(K)	303.15		308.15		313.15		318.15		323.15	
x_1	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
0.0000	0.99567	0.0000	0.99406	0.0000	0.99224	0.0000	0.99025	0.0000	0.98807	0.0000
0.0478	1.01551	−0.3930	1.01303	−0.3887	1.01049	−0.3875	1.00775	−0.3844	1.00466	−0.3763
0.1002	1.02762	−0.7792	1.02449	−0.7692	1.02109	−0.7563	1.01750	−0.7404	1.01386	−0.7256
0.1411	1.03254	−1.0265	1.02884	−1.0048	1.02501	−0.9840	1.02114	−0.9637	1.01723	−0.9443
0.1933	1.03404	−1.2238	1.03003	−1.1950	1.02605	−1.1730	1.02196	−1.1482	1.01775	−1.1205
0.2959	1.03247	−1.4403	1.02816	−1.4013	1.02395	−1.3739	1.01978	−1.3490	1.01557	−1.3231
0.3944	1.02843	−1.4636	1.02414	−1.4254	1.01997	−1.4022	1.01575	−1.3759	1.01157	−1.3521
0.4950	1.02379	−1.3592	1.01976	−1.3386	1.01561	−1.3181	1.01150	−1.2999	1.00742	−1.2834
0.5912	1.01994	−1.2096	1.01584	−1.1840	1.01177	−1.1710	1.00758	−1.1472	1.00343	−1.1251
0.7064	1.01520	−0.9058	1.01111	−0.8809	1.00705	−0.8705	1.00302	−0.8612	0.99903	−0.8531
0.8113	1.01165	−0.6040	1.00766	−0.5896	1.00370	−0.5911	0.99970	−0.5855	0.99566	−0.5729
0.8934	1.00904	−0.3272	1.00506	−0.3141	1.00111	−0.3183	0.99719	−0.3229	0.99330	−0.3281
1.0000	1.00647	0.0000	1.00258	0.0000	0.99858	0.0000	0.99461	0.0000	0.99067	0.0000

(BDEA) and + *n*-propylethanolamine (PEA) [21]; water + monoethylethanolamine (MEEA), + diethylethanolamine (DEEA) [22]; water + monoethanolamine (MEA), + monomethylethanolamine (MMEA), + DMEA [23]; densities, excess molar volumes, and partial molar volumes of water + MEA, + DEA and + TEA [24]; while further studies included the densities and viscosities of MDEA + triethyleneglycolmonometylether and + ethanol mixtures [25]. In other studies, Tremaine *et al.* [26] have measured the densities of aqueous AMP solutions and the heat capacities of aqueous solutions of MDEA and AMP;

Table 5. Experimental densities ρ (g cm^{-3}) and excess molar volumes V_m^E (cm^3 mol^{-1}) of the system BDEA (x_1) + water (x_2) for different molar ratios at different temperatures.

T(K)	303.15		308.15		313.15		318.15		323.15	
x_1	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
0.0000	0.99567	0.0000	0.99406	0.0000	0.99224	0.0000	0.99025	0.0000	0.98807	0.0000
0.0501	0.99960	−0.3777	0.99657	−0.3628	0.99356	−0.3518	0.99042	−0.3401	0.98717	−0.3283
0.0999	0.99743	−0.6120	0.99391	−0.5913	0.99034	−0.5717	0.98673	−0.5528	0.98307	−0.5348
0.1500	0.99488	−0.8014	0.99095	−0.7702	0.98711	−0.7453	0.98338	−0.7260	0.97939	−0.6984
0.2000	0.99206	−0.9398	0.98808	−0.9095	0.98414	−0.8824	0.98023	−0.8579	0.97634	−0.8364
0.3013	0.98666	−1.1118	0.98242	−1.0687	0.97835	−1.0374	0.97432	−1.0083	0.97032	−0.9818
0.3988	0.98179	−1.1470	0.97771	−1.1153	0.97366	−1.0861	0.96964	−1.0588	0.96566	−1.0338
0.4994	0.97750	−1.1002	0.97321	−1.0502	0.96924	−1.0287	0.96531	−1.0089	0.96120	−0.9711
0.6027	0.97357	−0.9675	0.96931	−0.9163	0.96536	−0.8977	0.96146	−0.8820	0.95756	−0.8646
0.7058	0.96996	−0.7473	0.96600	−0.7305	0.96207	−0.7151	0.95817	−0.7007	0.95430	−0.6875
0.8009	0.96752	−0.5671	0.96353	−0.5486	0.95958	−0.5312	0.95566	−0.5145	0.95171	−0.4886
0.8990	0.96495	−0.2967	0.96099	−0.2826	0.95713	−0.2797	0.95330	−0.2771	0.94950	−0.2751
1.0000	0.96267	0.0000	0.95879	0.0000	0.95494	0.0000	0.95112	0.0000	0.94733	0.0000

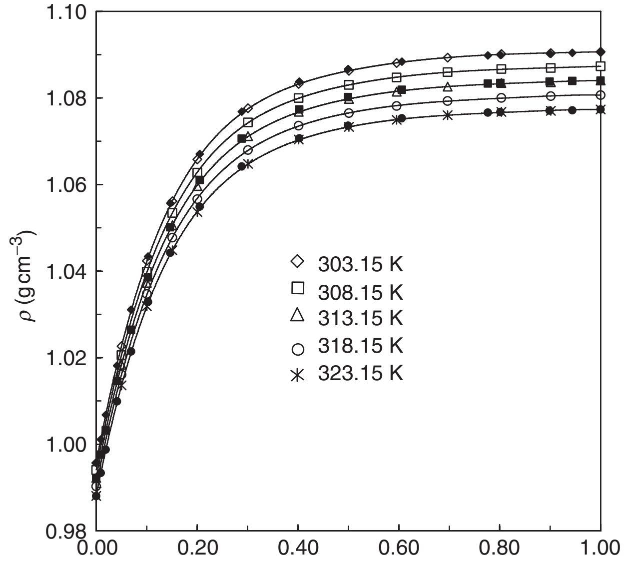

Figure 1. Densities for the aqueous solution of DEA as a function of mole fraction of DEA (x_1) at different temperatures: 303.15–323.15 K. The full lines represent fitting values with Equation (2). (◆) At 303.15 K, (■) at 313.15 K and (●) at 323.15 K represent the work of Mather *et al.* [24].

Hepler *et al.* [27] reported the volumetric properties of aqueous solutions of MDEA and EDEA; Li *et al.* [28] reported on the densities of water + DMEA, and + DEEA; Henni *et al.* [29,30] studied the density and viscosity of aqueous diisopropanolamine (DIPA) and also the densities, viscosities, and refractive indices for aqueous 2-(methylamino)ethanol (MAE)

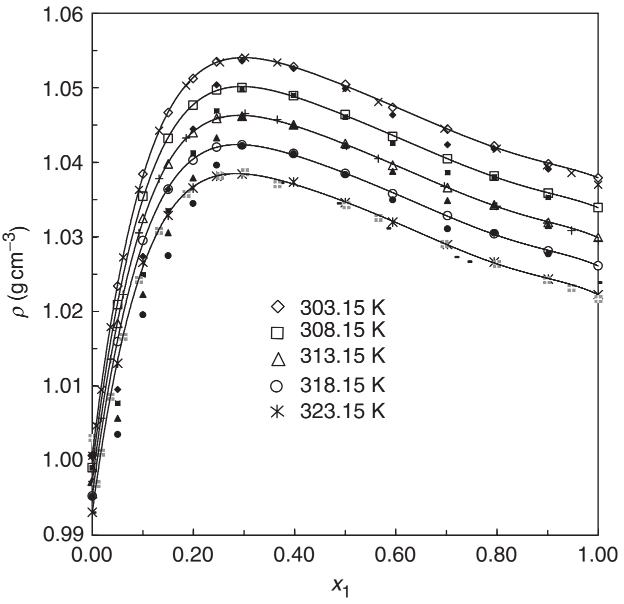

Figure 2. Densities for the aqueous solution of MDEA as a function of mole fraction of MDEA (x_1) at different temperatures: 303.15–323.15 K. The full lines represent fitting values with Equation (2). (◆) At 303.15 K, (■) at 308.15 K, (▲) at 313.15 K, (●) at 318.15 K and (–) at 323.15 K represent the work of Iglesias-Silva *et al.* [18] and (×) at 303.15 K, (+) at 313.15 K and (⁙) at 323.15 K represent the work of Hepler *et al.* [27].

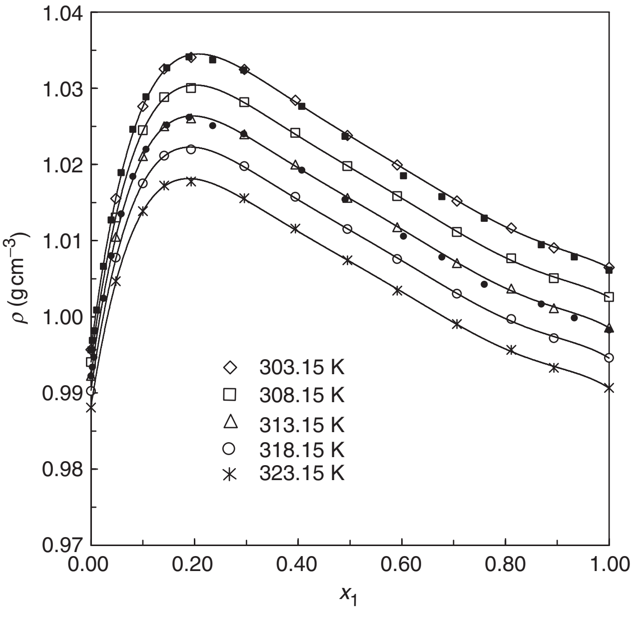

Figure 3. Densities for the aqueous solution of EDEA as a function of mole fraction of EDEA (x_1) at different temperatures: 303.15–323.15 K. The full lines represent fitting values with Equation (2). (■) At 303.15 K and (●) at 313.15 K represent the work of Hepler *et al.* [27].

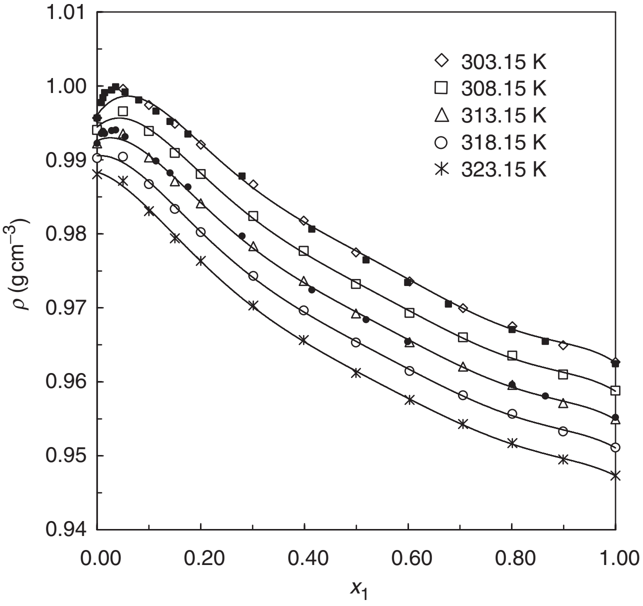

Figure 4. Densities for the aqueous solution of BDEA as a function of mole fraction of BDEA (x_1) at different temperatures: 303.15–323.15 K. The full lines represent fitting values with Equation (2). (■) At 303.15 K and (●) at 313.15 K represent the work of Mather *et al.* [21].

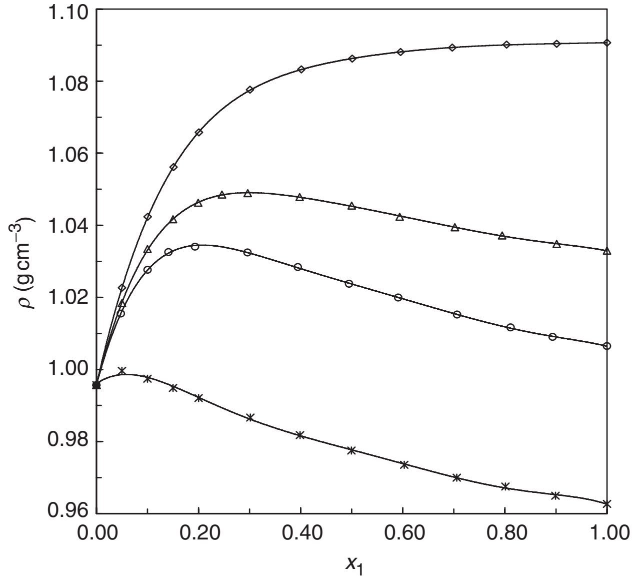

Figure 5. Comparison of densities for the solutions of DEA + W (◇), MDEA + W (△), EDEA + W (○) and BDEA + W (✳) as a function of mole fraction of diethanolamines (x_1) at the temperature 303.15 K. The full lines represent fitting values with Equation (2).

Table 6. Fitting coefficients a_i (g cm^{-3}) of polynomial Equation (2) and the value of r^2 for ρ (g cm^{-3}) for DEA (x_1) + water (x_2), MDEA (x_1) + water (x_2), EDEA (x_1) + water (x_2) and BDEA (x_1) + water (x_2) systems at different temperatures.

T (K)	a_0	a_1	a_2	a_3	a_4	a_5	a_6	r^2
DEA (x_1) + water (x_2)								
303.15	0.9957	0.6279	−1.9440	3.3985	−3.3999	1.8082	−0.3957	1.0000
308.15	0.9941	0.6175	−1.9324	3.4474	−3.5475	1.9510	−0.4428	1.0000
313.15	0.9923	0.6091	−1.9277	3.5167	−3.7414	2.1476	−0.5125	1.0000
318.15	0.9903	0.6033	−1.9414	3.6526	−4.0570	2.4512	−0.6183	1.0000
323.15	0.9881	0.5951	−1.9127	3.5917	−3.9735	2.3852	−0.5965	1.0000
MDEA (x_1) + water (x_2)								
303.15	0.9956	0.5649	−2.3453	5.0170	−6.0694	3.8955	−1.0254	0.9999
308.15	0.9940	0.5450	−2.2734	4.8772	−5.9151	3.8047	−1.0034	0.9999
313.15	0.9922	0.5296	−2.2388	4.8699	−5.9865	3.8964	−1.0379	0.9998
318.15	0.9902	0.5187	−2.2397	4.9787	−6.2385	4.1219	−1.1103	0.9998
323.15	0.9880	0.5083	−2.2365	5.0779	−6.4961	4.3722	−1.1966	0.9996
EDEA (x_1) + water (x_2)								
303.15	0.9957	0.5281	−2.6481	6.3196	−8.1952	5.4830	−1.4766	0.9998
308.15	0.9941	0.5093	−2.6265	6.4287	−8.5264	5.8136	−1.5902	0.9998
313.15	0.9923	0.4878	−2.5641	6.3754	−8.5769	5.9226	−1.6384	0.9998
318.15	0.9904	0.4649	−2.4792	6.2321	−8.4729	5.9093	−1.6500	0.9997
323.15	0.9882	0.4430	−2.3923	6.0750	−8.3417	5.8717	−1.6532	0.9997
BDEA (x_1) + water (x_2)								
303.15	0.9961	0.0969	−1.1017	3.5886	−5.7441	4.4919	−1.3651	0.9990
308.15	0.9944	0.0619	−0.8973	2.9761	−4.7827	3.7459	−1.1397	0.9991
313.15	0.9926	0.0335	−0.7514	2.5975	−4.2559	3.3729	−1.0343	0.9993
318.15	0.9905	0.0072	−0.6094	2.2087	−3.6877	2.9533	−0.9116	0.9995
323.15	0.9883	−0.0198	−0.4483	1.7329	−2.9551	2.3936	−0.7442	0.9996

solutions. Teja *et al.* [31] published the densities and viscosities of a series of ethanolamines. On the other hand, reports of Lee *et al.* [32–34] included the densities and viscosities of aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD); the densities, viscosities, and surface tensions of 2-amino-2-ethyl-1,3-propanediol (AEPD) + water; and the densities, viscosities, surface tensions, and refractive indices of triisopropanolamine (TIPA) + water. Also, Yoon *et al.* [35] measured the densities and viscosities of mixtures of 2-amino-2-methyl-1,3-propanediol (AMPD) + water; Lee and Lin [36] the densities and viscosities for MEA + water, + ethanol, and + 2-propanol; and Sandall *et al.* [37] reported on the density, viscosity, and surface tension of aqueous solutions of MDEA and aqueous solutions of DEA and DEA + MDEA.

Nevertheless, from the above survey it has been found that there is no report on the volumetric properties covering the series consisting of diethanolamines: DEA, MDEA, EDEA and BDEA. Therefore, in order to provide this new data to fill this gap we have measured the densities and calculated the excess molar volumes of the aqueous solutions of DEA, MDEA, EDEA and BDEA at different temperatures between 303.15 and 323.15 K in the whole range of composition. This would provide us with necessary information on the nature of interaction and also an opportunity to examine the effect of the size of alkyl groups attached to the N-atom of the alkanolamines under investigation.

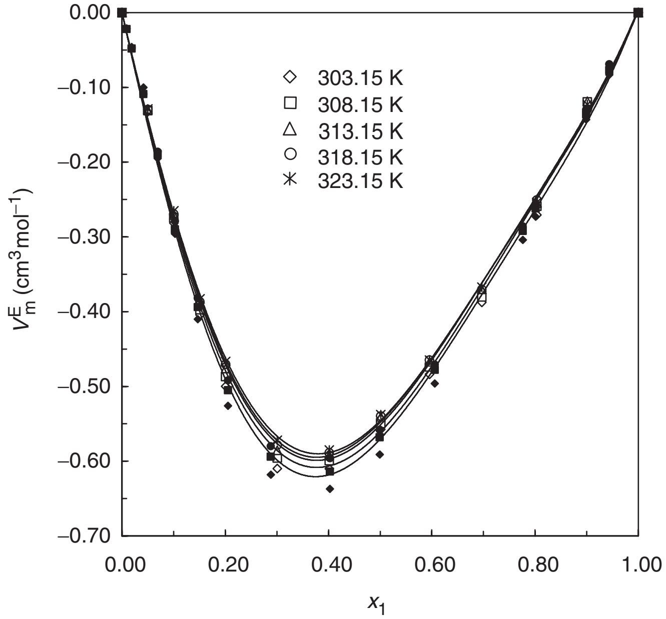

Figure 6. Excess molar volumes for the aqueous solution of DEA as a function of mole fraction of DEA (x_1) at different temperatures: 303.15–323.15 K. The full lines represent fitting values with Equation (3). (◆) At 303.15 K, (■) at 313.15 K and (●) at 323.15 K represent the work of Mather *et al.* [24].

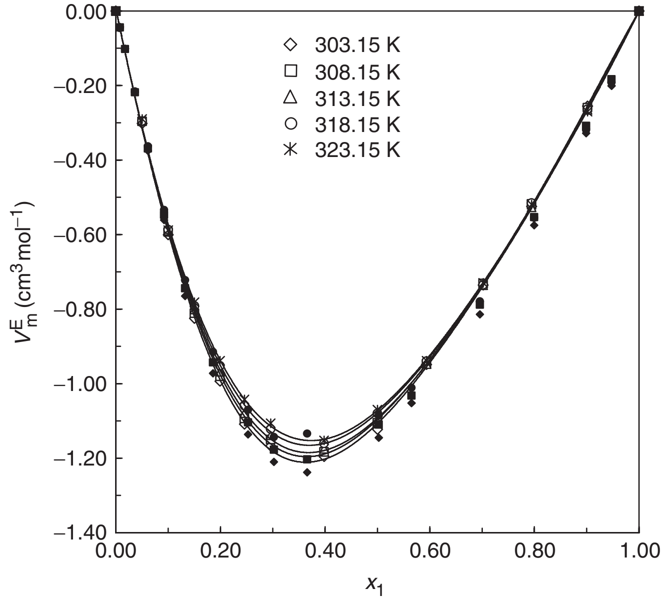

Figure 7. Excess molar volumes for the aqueous solution of MDEA as a function of mole fraction of DEA (x_1) at different temperatures: 303.15–323.15 K. The full lines represent fitting values with Equation (3). (◆) At 303.15 K (■) at 313.15 K and (●) at 323.15 K represent the work of Hepler *et al.* [27].

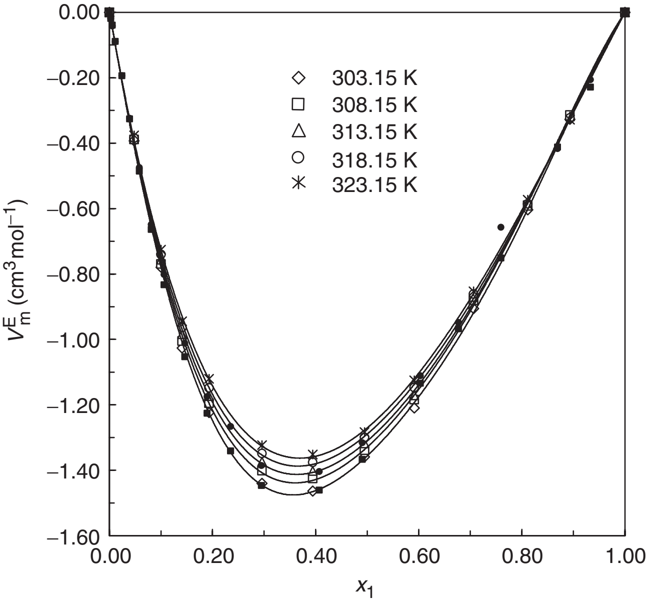

Figure 8. Excess molar volumes for the aqueous solution of EDEA as a function of mole fraction of EDEA (x_1) at different temperatures: 303.15–323.15 K. The full lines represent fitting values with Equation (3). (■) At 303.15 K and (●) at 313.15 K represent the work of Hepler *et al.* [27].

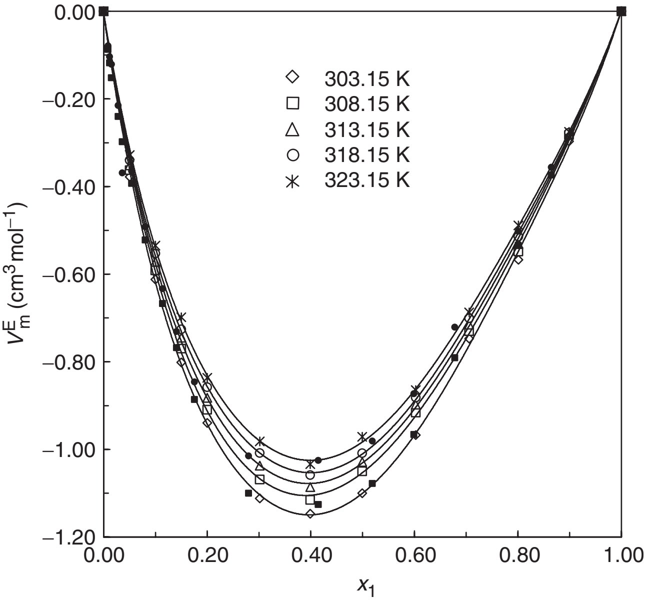

Figure 9. Excess molar volumes for the aqueous solution of BDEA as a function of mole fraction of BDEA (x_1) at different temperatures: 303.15–323.15 K. The full lines represent fitting values with Equation (3). (■) At 303.15 K and (●) at 313.15 K represent the work of Mather *et al.* [21].

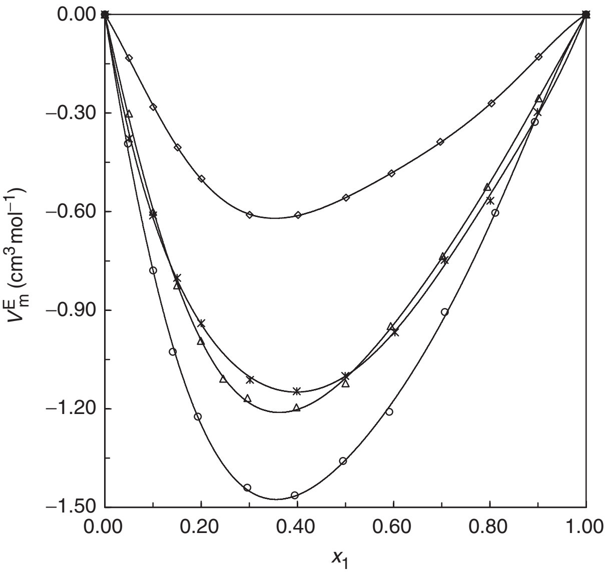

Figure 10. Comparison of excess molar volumes for the solutions of DEA + W (◇), MDEA + W (△), EDEA + W (○) and BDEA + W (∗) as a function of mole fraction of diethanolamines (x_1) at the temperature 303.15 K. The full lines represent fitting values with Equation (3).

2. Experimental

The liquids that were used to prepare the binary liquid mixtures with quoted purities: diethanolamine (99%), methyldiethanolamine (99%+), and ethyldiethanolamine (98%) were procured from Aldrich Chemical Co. Ltd, and *n*-butyldiethanolamine (>98%) was procured from Merck-Schuchardt. All these liquids were used without further purification. As a measure of purity check, the densities of the pure liquids are compared with the available literature values [21,24,27,31,38–41], which show satisfactory agreement, as found in Table 1.

Densities were measured by using a 5 mL pycnometer (MBL). All weighings were conducted on a Mettler Toledo SAG285 balance with an accuracy of ±0.00001 g. A thermostatically controlled water bath (controlled by a Thermo Haake DC 10 Thermostat), capable of maintaining the temperature constant up to ±0.05°C, was used in the studies.

The excess molar volume, V_m^E, was calculated by the following equation:

$$V_{\mathrm{m}}^{\mathrm{E}} = \frac{x_1 M_1 + x_2 M_2}{\rho_{\mathrm{mix}}} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right), \tag{1}$$

where ρ_{mix} is the measured density of the mixture, M_1, V_1 and x_1 are the molar mass, molar volume and the mole fraction of component 1, respectively, and M_2, V_2 and x_2 are the corresponding quantities of component 2 of the mixture.

3. Results and discussion

The densities of the DEA + W, MDEA + W, EDEA + W and BDEA + W systems in the whole range of composition at different temperatures (303.15–323.15 K) are displayed

Table 7. Fitting coefficients a_i (cm^3 mol^{-1}) of polynomial Equation (3) and the value of r^2 for V_m^E(cm^3 mol^{-1}) for DEA(x_1) + water (x_2), MDEA (x_1) + water (x_2), EDEA (x_1) + water (x_2) and BDEA (x_1) + water (x_2) systems at different temperatures.

T(K)	a_1	a_2	a_3	a_4	a_5	a_6	r^2
DEA (x_1) + water (x_2)							
303.15	−2.4579	−7.4859	53.5204	−102.6230	86.0237	−26.9772	0.9999
308.15	−2.4557	−6.6247	49.3473	−95.0412	80.0547	−25.2803	0.9999
313.15	−2.4657	−5.7204	44.6149	−85.2194	70.9541	−22.1633	0.9999
318.15	−2.5688	−3.7870	35.1262	−65.4975	52.4501	−15.7233	0.9999
323.15	−2.5132	−4.1479	36.6975	−69.2121	56.4607	−17.2847	0.9999
MDEA (x_1) + water (x_2)							
303.15	−6.6424	4.7597	29.2131	−64.9110	53.9447	−16.3646	0.9996
308.15	−6.5762	5.1656	26.3947	−59.0826	48.7238	−14.6265	0.9997
313.15	−6.5749	6.0225	22.2687	−51.6670	42.7061	−12.7562	0.9997
318.15	−6.6472	7.6671	15.8433	−41.3327	35.1495	−10.6812	0.9997
323.15	−6.7194	9.5607	6.9066	−23.8592	19.5486	−5.4382	0.9996
EDEA (x_1) + water (x_2)							
303.15	−9.2917	13.8599	17.6744	−66.0588	67.8378	−24.0225	0.9996
308.15	−9.3691	17.0165	3.2403	−39.3405	45.4827	−17.0305	0.9996
313.15	−9.3292	18.4495	−4.4856	−23.8124	31.4369	−12.2596	0.9996
318.15	−9.2163	19.1606	−9.7453	−11.9327	19.8115	−8.0782	0.9997
323.15	−9.1036	20.1282	−16.7487	3.9298	4.4386	−2.6450	0.9998
BDEA (x_1) + water (x_2)							
303.15	−8.4657	28.0616	−62.7241	95.6409	−76.7633	24.2527	0.9994
308.15	−7.9743	24.3674	−48.2304	68.2585	−52.8856	16.4669	0.9993
313.15	−7.7848	24.6497	−52.2619	77.7876	−61.9341	19.5455	0.9995
318.15	−7.6017	24.7118	−54.9387	84.3461	−68.1589	21.6428	0.9997
323.15	−7.2923	23.1270	−50.3949	77.1845	−62.5488	19.9247	0.9996

in Tables 2–5. Figures 1–4 show the density curves at different temperatures for aqueous solutions of DEA, MDEA, EDEA and BDEA, respectively, as a function of mole fraction of the respective alkanolamine. The comparative variation of densities of aqueous diethanolamines at 303.15 K is depicted in Figure 5. The density values for all systems are fitted with six-degree polynomial equations of the following form:

$$\rho\ (\mathrm{g\ cm^{-3}}) = \sum_{i=0}^{n} a_i x_1^i, \qquad (2)$$

where x_1 is the mole fraction of alkanolamine, a_i (g cm^{-3}) the regression coefficient and n the degree of polynomial. For each system, the values of ρ fit to Equation (2) well for $n = 6$. The coefficients a_i of Equation (2) and relevant values of r^2 for the density of all the four systems at various temperatures (303.15–323.15 K) obtained by the least-squares method are listed in Table 6. All the values of r^2 are found to be very close to unity.

The measured density data at different temperatures for the system DEA + W are compared with the data reported by Mather *et al.* [24]; for MDEA + W with the data reported by Iglesias-Silva *et al.* [18] and Hepler *et al.* [27]; for EDEA + W with the data of Hepler *et al.* [27]; and for BDEA + W with the data of Mather *et al.* [21]. All the density data obtained in this study are in good agreement with the literature values.

The densities of the pure diethanolamines vary as DEA > MDEA > EDEA > BDEA, apparently in the reverse order of the molar masses of the compounds. The densities of the diethanolamines are assumed to be related to their strength of association. On examination of the structures of diethanolamines, one can easily anticipate that amongst all the amines of this series, DEA is the most associated due to its having the lowest steric effect. The obvious consequence of such a steric effect is reflected in the observed order of densities of the other diethanolamines.

From all the density graphs it is found that ρ for the DEA + W system rises sharply initially on addition of DEA. Following this, the rate of increment slows down and finally the values level off as the composition approaches the pure state of DEA. In the cases of the MDEA + W and EDEA + W systems, ρ increases with an accelerated rate, initially showing maxima at ~0.30 and ~0.20 mole fraction of the respective amines, and then declines fairly regularly with the further addition of the alkanolamines. But density curves, especially at lower temperatures for the aqueous solution of BDEA, show peculiar behaviour. After a very initial short rising, curves pass through maxima then decline with a more or less convex nature of curvature with the addition of BDEA. Mather *et al.* [21] also found similar behaviour in the aqueous BDEA solution.

The observed variation of densities of aqueous solutions of these diethanolamines is DEA + W > MDEA + W > EDEA + W > BDEA + W. Hepler *et al.* [27] studied aqueous solutions of DEA, MDEA, and EDEA and also found a similar variational trend. This order is assumed to be related to the relative strength of self- as well as cross-association, which is related to the steric effect, as mentioned above. The variation of the steric effects of these alkanolamines may be depicted to depend on the following order of N-substituted atom and group:

$$-CH_2\,CH_2\,CH_2\,CH_3 > -CH_2\,CH_3 > -CH_3 > -H.$$

Values of V_m^E for aqueous solutions of DEA, MDEA, EDEA and BDEA at different temperatures between 303.15 and 323.15 K are listed in Tables 2–5 and are represented by Figures 6–9, respectively, as a function of the mole fraction of the corresponding alkanolamines. The V_m^E values as compared at 303.15.K are given by Figure 10. The observed values of excess molar volumes for all systems are well fitted with the six-degree polynomial equations of the following form:

$$V_{\mathrm{m}}^{\mathrm{E}}(\mathrm{cm}^3\ \mathrm{mol}^{-1}) = \sum_{i=1}^{n} a_i x_1^i, \tag{3}$$

where x_1 is the mole fraction of alkanolamine, a_i (cm^3 mol^{-1}) the regression coefficient and n the degree of polynomial. For each of the systems the values of V_m^E fit to Equation (3) well for $n = 6$. The coefficients a_i of Equation (3) and relevant values of r^2 for V_m^E of all the four systems at various temperatures (303.15–323.15 K) obtained by the least-squares method are listed in Table 7. The values of r^2 are found to be very close to unity.

The excess molar volumes of the system DEA + W agreed well with the data of Mather *et al.* [24]; MDEA + W and EDEA + W with Hepler *et al.* [27]; and BDEA + W with the data of Mather *et al.* [21] as well. V_m^E values for all the systems are negative in the whole range of composition at all temperatures, which is a common observation for the aqueous solutions of other alkanolamines. The negative excess molar volumes for all the aqueous diethanolamines solutions are also significantly large.

The negative excess molar volumes in the present systems indicate that there is volume contraction in each system, and this can be explained by the large difference in the molar volumes. Pal and Sing [42] suggested that volume contraction was particularly due to the ability of the alkanolamines with –OH groups to form H-bonds with water molecules. However, another interpretation was that such a marked change in V_m^E might also be due to the accommodation of the non-aqueous molecules within the structured water lattice/ void space. Minima having significantly large depth for the DEA + W, MDEA + W and BDEA + W systems occurred at ~0.35 mole fraction of the respective alkanolamines and those for the BDEA + W system at ~0.40 mole fraction of BDEA. The depth of minima varies as EDEA + W > MDEA + W > BDEA + W > DEA + W. Similarly, variation in the depth of minima for the aqueous solutions of DEA, MDEA and EDEA was found by Hepler *et al.* [27]. However, occurrence of such deep minima may additionally be attributed to the hydrophobicity of the hydrocarbon groups attached to N-atoms of the alkanolamine molecules. The more the hydrophobicity, the greater the depth of the minima. However, BDEA + W does not follow this order, which indicates that there should be a limiting size of alkyl groups attached to the N-atom to affect the excess molar volume of aqueous alkanolamine solutions. Mather *et al.* [21] argued the same when considering the aqueous solutions of MEA, MMEA, MEEA and PEA. In the earlier works of Mather *et al.* [21] and Alvarez *et al.* [43, 44], it was found that there is a dependency between the excess molar volumes of water + alkylethanolamines mixtures and the size of the substituted alkyl group on the nitrogen atom of alkylethanolamines. Accordingly, the values of excess molar volume become more negative by increasing the size of the alkyl group attached to the nitrogen atom, but for PEA, V_m^E becomes less negative. This may all be explained as follows. An alkyl group having limiting size has the highest ability to be interstitially accommodated. On top of this, the ability of alkyl groups to incorporate in structural water decreases, which eventually fails to cause further volume contraction even at increasing hydrophobicity.

From the above discussion, a conclusion may thus be drawn out that the effect of alkyl groups (attached to N-atoms of alkanolamines) contributing negatively towards excess molar volumes should follow the trend:

$$-CH_2\,CH_2\,CH_2\,CH_3 \text{ or } -CH_2\,CH_2\,CH_3 < -CH_2\,CH_3 > -CH_3.$$

The effect of temperature on V_m^E is observed to be very small, and V_m^E becomes less negative as the temperature increases, which is a common feature for different alkanolamine solutions with water. This is because both self-association and cross-association of the H-bonds decrease with increasing temperature, which leads to certain positive contributions to V_m^E and hence, the overall V_m^E becomes less negative.

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