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Volumetric properties of binary mixtures of water with ethanolamine alkyl derivatives

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Abstract

Accurate densities for binary mixtures of water + *N,N*-dimethylethanolamine, and + *N,N*-diethylethanolamine were measured at different temperatures. The molar excess volumes V^E of the mixtures and the apparent molar volumes of both components have been derived as functions of the composition. The V^E values are negative over the entire composition range at various temperatures. Compared with monoethanolamine itself, the introduction of two methyl or ethyl groups into it leads to more negative V^E values. The results are discussed in terms of specific interactions present in the binary mixtures and a comparative study is made between the methyl and ethyl ethanolamine derivatives.

Keywords: Binary system; Diethylethanolamine; Dimethylethanolamine; Excess molar volume; Water

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1. Introduction

Although thermodynamic properties for pure ethanolamine (EA) alkyl derivatives [1] and their aqueous binary mixtures [2] have been studied, a systematic study of the volumetric properties for the mixtures, water + *N,N*-dimethylethanolamine (DMEA), and + *N,N*-diethylethanolamine (DEEA) at various temperatures was not performed until recently. This work reports the excess molar volumes V^E and apparent molar volumes, Φ_v of the two binary mixtures at four temperatures. The

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molecule of EA derivative contains two kinds of polar groups, hydroxyl and amino groups, leading to complicated intermolecular interactions with water. The contributions of specific molecular interactions to V^E are also analysed. We have undertaken a further study of V^E and Φ_v for these mixtures, and a comparative study is made for DMEA, DEEA and MEA (monoethanolamine) from our earlier work [3].

2. Experimental

The molar excess volumes of mixing were calculated from experimental density data. The solutions for the measurement of densities were prepared by weighing in specified mixing tubes similar to those of Takenaka et al. [4]. The maximum uncertainty in the mole fraction is 10^{-4}. Densities of mixtures of DMEA or DEEA with water were measured at 293.15, 298.15, 303.15 and 313.15 K using an Anton Paar DMA 602 digital densimeter. The accuracies of most of our densities were about $\pm 3 \times 10^{-6}$ g cm^{-3}. The temperatures of the thermostatic bath were stable to ± 0.005 K, using circulating water from a Heto thermostat. Calibrations were carried out with doubly distilled water and dry air. The densities of water and dry air needed for calibration at different temperatures (ITS−90) were taken from the literature [5,6].

DMEA and DEEA (c.p. grade) were further purified over potassium hydroxide pellets for more 48 h, and then by fractional distillation twice through a 1 m column under reduced pressure, with the middle fraction being collected. The mass fractions of water in DMEA and DEEA after distillation by Karl–Fischer titration were 0.0002 and 0.0003, respectively. All solutions were freshly prepared with doubly distilled water in Teflon stoppered flasks. The observed densities of pure DMEA and DEEA are 0.88314 (298.10 K) and 0.87954 (298.15 K), respectively, and our values agree with the literature [1].

3. Results

The excess molar volumes V^E of the mixtures of ethanolamine derivative with water were calculated using the equation

$$V^E = x_1 M_1\left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + x_2 M_2\left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \tag{1}$$

where x_i and M_i denote the mole fraction and molar mass of water ($i = 1$) or ethanolamine derivative ($i = 2$), respectively, and ρ, ρ_1 and ρ_2 are the densities of the solution and of the pure components.

The apparent molar volume of component 1, $\Phi_{v,1}$, is derived from

$$\Phi_{v,1} = \frac{M_1}{\rho} + \frac{x_2}{x_1} M_2\left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \tag{2}$$

A similar equation is employed for component 2.

Table 1
Experimental densities (g cm^{-3}), excess molar volumes of mixtures (cm^3 mol^{-1}) and apparent molar volumes (cm^3 mol^{-1}) of the component for water + DMEA and water + DEEA

x_1	ρ	V^E	$\Phi_{v,1}$	$\Phi_{v,2}$
Water + *N*,*N*-dimethylethanolamine 293.15 K				
0.0000	0.88747	0		100.44
0.0295	0.88916	−0.120	13.96	100.32
0.0736	0.89181	−0.295	14.04	100.12
0.1325	0.89556	−0.513	14.17	99.85
0.1786	0.89879	−0.683	14.22	99.61
0.2495	0.90419	−0.926	14.34	99.21
0.3009	0.90853	−1.092	14.42	98.88
0.3454	0.91259	−1.225	14.50	98.57
0.4045	0.91845	−1.384	14.62	98.12
0.4521	0.92364	−1.496	14.74	97.71
0.5120	0.93074	−1.609	14.91	97.14
0.5766	0.93919	−1.688	15.12	96.45
0.5809	0.93981	−1.693	15.13	96.40
0.6324	0.94722	−1.715	15.34	95.78
0.7279	0.96228	−1.634	15.80	94.44
0.8023	0.97481	−1.432	16.26	93.20
0.8463	0.98194	−1.232	16.59	92.42
0.9156	0.99045	−0.752	17.23	91.53
0.9476	0.99254	−0.459	17.56	91.67
0.9742	0.99428	−0.210	17.83	92.33
0.9865	0.99568	−0.102	17.94	92.87
0.9959	0.99729	−0.029	18.02	93.34
1.0000	0.99820	0	18.05	
298.10 K				
0.0000	0.88314	0		100.93
0.0354	0.88520	−0.145	13.96	100.78
0.0703	0.88730	−0.282	14.06	100.63
0.1260	0.89087	−0.494	14.15	100.37
0.1733	0.89417	−0.668	14.21	100.12
0.2523	0.90018	−0.937	14.35	99.68
0.3012	0.90433	−1.095	14.43	99.37
0.3457	0.90842	−1.229	14.51	99.06
0.4081	0.91463	−1.392	14.66	98.58
0.4622	0.92057	−1.513	14.79	98.12
0.5063	0.92587	−1.596	14.92	97.70
0.5531	0.93181	−1.656	15.08	97.23
0.5842	0.93634	−1.700	15.16	96.84
0.6338	0.94330	−1.705	15.38	96.28
0.7076	0.95477	−1.648	15.74	95.30
0.7526	0.96240	−1.567	15.99	94.60
0.8199	0.97386	−1.341	16.43	93.49
0.8694	0.98173	−1.079	16.83	92.67
0.9107	0.98701	−0.781	17.21	92.18
0.9405	0.98976	−0.522	17.51	92.16

Table 1 (continued)

x_1	ρ	V^E	$\Phi_{v,1}$	$\Phi_{v,2}$
Water + *N*,*N*-dimethylethanolamine				
0.9679	0.99205	−0.267	17.79	92.60
0.9891	0.99476	−0.083	17.98	93.36
0.9922	0.99533	−0.058	18.01	93.50
0.9969	0.99630	−0.023	18.05	93.75
1.0000	0.99704	0	18.07	
303.15 K				
0.0000	0.87878	0		101.43
0.0434	0.88130	−0.175	14.06	101.25
0.0957	0.88382	−0.304	14.92	101.10
0.1906	0.89113	−0.733	14.25	100.53
0.2641	0.89686	−0.978	14.39	100.10
0.3074	0.90059	−1.114	14.47	99.82
0.3513	0.90467	−1.244	14.55	99.52
0.4258	0.91223	−1.431	14.73	98.94
0.4640	0.91649	−1.512	14.84	98.61
0.5089	0.92187	−1.592	14.97	98.19
0.5607	0.92857	−1.657	15.14	97.66
0.5966	0.93354	−1.682	15.27	97.26
0.6342	0.93904	−1.689	15.43	96.82
0.7129	0.95148	−1.626	15.81	95.77
0.7545	0.95851	−1.543	16.05	95.15
0.8251	0.97076	−1.298	16.52	94.01
0.8749	0.97894	−1.028	16.92	93.22
0.9142	0.98432	−0.743	17.28	92.77
0.9451	0.98771	−0.477	17.59	92.75
0.9703	0.99043	−0.247	17.84	93.11
0.9886	0.99314	−0.088	18.00	93.70
0.9927	0.99397	−0.055	18.04	93.85
0.9965	0.99478	−0.026	18.07	94.02
1.0000	0.99565	0	18.09	
313.15 K				
0.0000	0.87025	0		102.43
0.0413	0.87272	−0.175	13.92	102.25
0.0826	0.87528	−0.340	14.04	102.06
0.1362	0.87883	−0.544	14.16	101.80
0.1925	0.88287	−0.749	14.26	101.50
0.2682	0.88883	−1.001	14.43	101.06
0.3039	0.89194	−1.114	14.49	100.83
0.3518	0.89636	−1.251	14.60	100.50
0.4276	0.90412	−1.440	14.79	99.91
0.4652	0.90828	−1.513	14.90	99.60
0.5105	0.91371	−1.588	15.05	99.18
0.5633	0.92052	−1.646	15.23	98.66
0.5923	0.92460	−1.668	15.34	98.34
0.6366	0.93104	−1.671	15.53	97.83
0.7138	0.94328	−1.598	15.92	96.85
0.7570	0.95063	−1.503	16.17	96.24

Table 1 (continued)

x_1	ρ	V^E	$\Phi_{v,1}$	$\Phi_{v,2}$
Water + *N*,*N*-dimethylethanolamine				
0.8225	0.96235	−1.276	16.60	95.24
0.8748	0.97158	−1.001	17.01	94.44
0.9150	0.97815	−0.722	17.37	93.94
0.9458	0.98247	−0.464	17.67	93.87
0.9686	0.98583	−0.264	17.88	94.04
0.9888	0.98949	−0.089	18.07	94.49
0.9923	0.99027	−0.060	18.10	94.61
0.9959	0.99113	−0.031	18.12	94.75
1.0000	0.99221	0	18.16	
Water + *N*,*N*-diethylethanolamine				
293.15 K				
0.0000	0.88420	0		132.54
0.0281	0.88570	−0.155	12.53	132.38
0.0796	0.88852	−0.417	12.81	132.09
0.1258	0.89121	−0.640	12.96	131.81
0.1937	0.89549	−0.947	13.16	131.37
0.2533	0.89954	−1.187	13.36	130.95
0.3043	0.90337	−1.381	13.51	130.56
0.3590	0.90775	−1.559	13.70	130.11
0.4128	0.91244	−1.708	13.91	129.63
0.4514	0.91602	−1.796	14.07	129.27
0.5184	0.92279	−1.905	14.37	128.58
0.5791	0.92972	−1.962	14.66	127.88
0.6579	0.93965	−1.936	15.10	126.88
0.7086	0.94686	−1.863	15.42	126.15
0.7676	0.95614	−1.709	15.82	125.19
0.8042	0.96258	−1.576	16.09	124.49
0.8567	0.97268	−1.322	16.50	123.32
0.9017	0.98214	−1.033	16.90	122.03
0.9273	0.98753	−0.827	17.16	121.16
0.9506	0.99176	−0.599	17.42	120.42
0.9760	0.99467	−0.291	17.75	120.42
0.9856	0.99563	−0.167	17.88	120.90
0.9903	0.99625	−0.109	17.94	121.26
0.9949	0.99704	−0.055	17.99	121.68
1.0000	0.99820	0	18.05	
298.15 K				
0.0000	0.87954	0		133.24
0.0281	0.88098	−0.146	12.88	133.09
0.0796	0.88384	−0.413	12.88	132.80
0.1258	0.88651	−0.634	13.03	132.52
0.1937	0.89082	−0.944	13.19	132.07
0.2533	0.89488	−1.184	13.40	131.66
0.3043	0.89873	−1.378	13.54	131.26
0.3590	0.90314	−1.557	13.73	130.81
0.4128	0.90782	−1.704	13.94	130.34
0.4514	0.91183	−1.826	14.02	129.91

Table 1 (continued)

x_1	ρ	V^E	$\Phi_{v,1}$	$\Phi_{v,2}$
Water + *N*,*N*-diethylethanolamine				
0.5184	0.91821	−1.899	14.41	129.30
0.5773	0.92491	−1.949	14.69	128.63
0.6586	0.93517	−1.918	15.16	127.62
0.7045	0.94172	−1.852	15.44	126.98
0.7643	0.95117	−1.699	15.84	126.03
0.8048	0.95836	−1.553	16.14	125.29
0.8567	0.96856	−1.299	16.55	124.18
0.9017	0.97840	−1.013	16.94	122.94
0.9273	0.98420	−0.811	17.19	122.08
0.9506	0.98900	−0.590	17.45	121.32
0.9760	0.99288	−0.292	17.77	121.11
0.9856	0.99416	−0.169	17.90	121.47
0.9903	0.99491	−0.111	17.96	121.76
0.9949	0.99580	−0.056	18.01	122.11
1.0000	0.99704	0	18.07	
303.15 K				
0.0000	0.87482	0		133.96
0.0411	0.87701	−0.220	12.74	133.73
0.0921	0.87989	−0.481	12.87	133.43
0.1339	0.88233	−0.676	13.05	133.18
0.1920	0.88603	−0.939	13.20	132.80
0.2577	0.89054	−1.205	13.42	132.34
0.3048	0.89407	−1.379	13.57	131.90
0.3604	0.89861	−1.564	13.76	131.52
0.4114	0.90303	−1.700	13.96	131.07
0.4511	0.90673	−1.787	14.13	130.70
0.5140	0.91308	−1.887	14.42	130.08
0.5770	0.92016	−1.935	14.74	129.39
0.6316	0.92699	−1.930	15.04	128.72
0.7080	0.93763	−1.828	15.51	127.70
0.7671	0.94716	−1.672	15.91	126.78
0.8036	0.95369	−1.536	16.18	126.14
0.8562	0.96445	−1.289	16.59	125.00
0.9033	0.97503	−0.986	17.00	123.77
0.9274	0.98087	−0.799	17.23	122.96
0.9509	0.98627	−0.580	17.48	122.16
0.9763	0.99094	−0.288	17.80	121.81
0.9868	0.99263	−0.156	17.94	122.17
0.9913	0.99354	−0.101	17.99	122.33
0.9957	0.99452	−0.049	18.04	122.56
1.0000	0.99565	0	18.09	
313.15 K				
0.0000	0.86556	0		135.40
0.0411	0.86774	−0.220	12.82	135.17
0.0921	0.87064	−0.484	12.90	134.86
0.1339	0.87309	−0.681	13.07	134.61
0.1920	0.87683	−0.947	13.22	134.22

Table 1 (continued)

x_1	ρ	V^E	$\Phi_{v,1}$	$\Phi_{v,2}$
Water + *N,N*-diethylethanolamine				
0.2577	0.88134	−1.211	13.46	133.76
0.3048	0.88481	−1.376	13.64	133.42
0.3604	0.88934	−1.559	13.83	132.96
0.4114	0.89380	−1.696	14.03	132.51
0.4511	0.89753	−1.783	14.20	132.15
0.5140	0.90383	−1.874	14.51	131.54
0.5770	0.91089	−1.915	14.84	130.87
0.6583	0.92131	−1.880	15.30	129.89
0.7072	0.92834	−1.798	15.61	129.26
0.7654	0.93791	−1.646	16.01	128.38
0.8036	0.94463	−1.491	16.30	127.80
0.8562	0.95614	−1.258	16.69	126.65
0.9033	0.96742	−0.958	17.10	125.49
0.9274	0.97379	−0.774	17.32	124.74
0.9509	0.98020	−0.566	17.56	123.87
0.9763	0.98644	−0.289	17.86	123.19
0.9868	0.98876	−0.160	17.99	123.26
0.9913	0.98983	−0.104	18.05	123.38
0.9957	0.99095	−0.051	18.10	123.62
1.0000	0.99221	0	18.16	

Experimental results for the densities of mixtures and the excess molar volumes obtained at different temperatures are reported in Table 1. At each temperature, the experimental V^E values were fitted using the Redlich–Kister equation

$$V^E = x_2(1 - x_2) \sum_{j=0}^{n} A_j(1 - 2x_2)^j \tag{3}$$

where the parameters A_j were obtained by the method of least squares. A_j and the corresponding standard deviations are given in Table 2. Fig. 1 shows the experimental values of V^E as functions of x_1, together with fitted curves calculated by Eq. (3). As the curves for each mixture at the temperatures studied nearly coincide, only curves for two temperatures are plotted in Fig. 1 for the mixtures. The V^E curve of MEA with water at 313.15 K [3] is also given for comparison.

Table 1 presents the apparent molar volumes of both components. Apparent molar volumes of solutes are plotted in Fig. 2.

4. Discussion

4.1. Excess molar volume

For the water(1) + EA derivative(2) mixtures, V^E values are all negative over the entire concentration range, and in the two cases the variations of V^E vs. x_1 show

Table 2
Coefficients A_j and standard deviations s for representation of V^E for ethanolamine derivative systems at various temperatures

	Water + DMEA				Water + DEEA			
	293.15 K	298.10 K	303.15 K	313.15 K	293.15 K	298.15 K	303.15 K	313.15 K
A_0	−6.382	−6.350	−6.336	−6.307	−7.576	−7.576	−7.447	−7.410
A_1	−3.494	−3.459	−3.394	−3.202	−2.724	−2.449	−2.322	−2.119
A_2	−0.423	−1.090	0.505	−0.567	1.790	1.895	−2.377	−1.619
A_3	0.945	1.140	0.950	1.784	−5.166	−6.850	−8.927	−8.717
A_4	−4.962	−1.038	−15.452	−2.843	−29.940	−27.332	9.435	5.353
A_5	−5.554	−5.222	3.230	−6.167	23.272	27.315	39.582	38.299
A_6	6.179	−0.032	38.365	3.623	104.403	93.431	−21.241	−12.691
A_7	6.831	6.147	−23.664	6.141	−44.250	−46.482	−68.829	−65.304
A_8		2.859	−25.183		−151.823	−135.618	12.799	7.242
A_9			23.731		26.210	25.320	38.092	35.139
A_{10}					75.668	67.796		
$s/(\mathrm{cm^3\ mol^{-1}})$	0.0036	0.0029	0.0052	0.0034	0.0068	0.0070	0.0070	0.0068

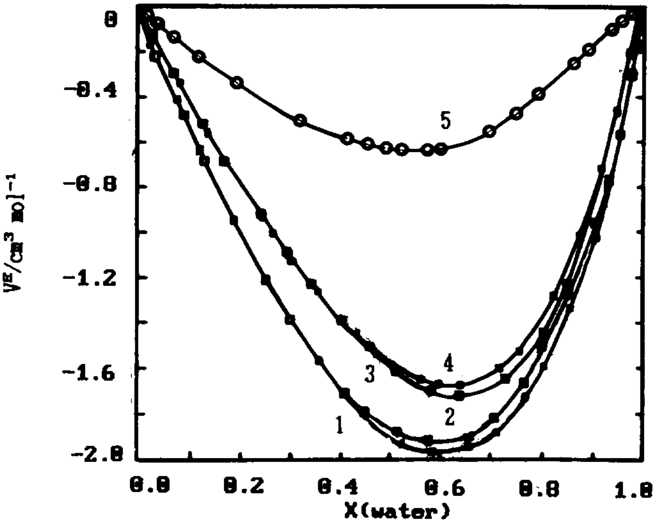

Fig. 1. Experimental values of V^E as functions of x, and fitted curves calculated using Eq. (3): 1, DEEA + H_2O at 293.15 K; 2, DEEA + H_2O at 313.15 K; 3, DMEA + H_2O at 293.15 K; 4, DMEA + H_2O at 313.15 K; 5, MEA + H_2O at 313.15 (for comparison, from [3]).

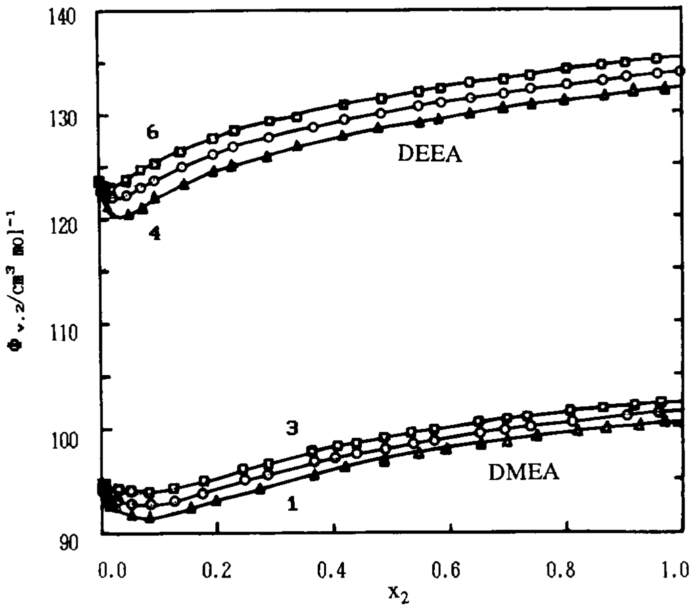

Fig. 2. Apparent molar volumes of DMEA + H_2O and DEEA + H_2O: 1, 4, at 293.15 K; 2, 5, at 303.15 K; 3, 6, at 313.15 K.

characteristic minima at various temperatures. For each V^E vs. x_1 curve, the minimum value appears in the water-rich region at about $x_1 = 0.6$. In Fig. 1, V^E decreases drastically with the introduction of two methyl or ethyl groups as compared with MEA, which indicates the dominant role of N · · · HO H-bonding in unlike molecular interactions. The variations of V^E with composition and temperature for the two mixtures reveal a similar trend.

With the introduction of methyl or ethyl groups, the hydrophobicity of EA increases, causing an increase in volume; the breaking of the self-associates 1–1 and 2–2 when mixed also gives an increase in V^E. However the negative contributions to V^E are due to the formation of a strong cross H-bond between unlike molecules. This can be inferred experimentally from the fact that the negative contribution is predominant, so the value of V^E is negative.

The experimental V^E for these aqueous mixtures follows the order V^E(DEEA) < V^E(DMEA) < V^E(MEA).

Generally, a strong cross H-bonding between H_2O and EA derivative is the most important factor in determining the value of V^E. However, evidence for the influence of hydrophobic interaction is clearly seen in the minimum value of the V^E vs. x_1 curve, which appears in the water-rich region.

From Fig. 1, the V^E values become slightly more negative with the decrease in temperature for the same mixture. It is known that H-bonds of self-association and cross-association decrease with increasing temperature, which leads to a positive contribution to V^E. Although the formation of H-bonds is still predominant, V^E values show a slight increase as compared with the lower temperature. Because the temperature dependence of V^E is smaller in this work, V^E values at two temperatures do not exhibit an appreciable difference.

4.2. *Apparent molar volume*

It is apparent from the results reported in Table 1 that $\Phi_{v,DEEA} > \Phi_{v,DMEA}$ at the same temperature. The curves in Fig. 2 each have a minimum. The position of the minimum changes with change in the solute structure. The Φ_v values show an increase with temperature because the densities of the binary mixtures decrease with temperature. At 298.15 K, Touhara and coworkers [2] reported an estimated value of the partial molar excess volume, $(V_2^E)_{x_2 \to 0}$ of DMEA in water (-7.5 cm^3 mol^{-1}). Because the partial molar excess volume at infinite dilution $(V_2^E)_{x_2 \to 0}$ equals the difference between the partial molar volume of DMEA in aqueous mixture and the molar volume of pure DMEA, our value at this temperature is -7.045 cm^3 mol^{-1}, calculated from Maham et al.'s method [7], $(V_2^E)_{x_2 \to 0} = \Sigma A_j$ (A_j, Redlich–Kister parameters in Table 2), which agrees with that of Touhara [2].

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