International Journal of Thermophysics, Vol. 28, No. 4, August 2007 (© 2007)
DOI: 10.1007/s10765-007-0204-0

Densities and Volumetric Properties of Binary Mixtures of Aniline with 1-Propanol, 2-Propanol, 2-Methyl-1-Propanol, and 2-Methyl-2-Propanol at Temperatures from 293.15 to 318.15 K

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Received January 12, 2007

The densities of binary mixtures of aniline with 1-propanol, 2-propanol, 2-methyl-1-propanol, and 2-methyl-2-propanol were measured over the entire composition range, along with the pure components, at temperatures of 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15 K and atmospheric pressure. Using the experimental data, the excess molar volumes, V_m^E, and the temperature coefficients of the excess molar volume, $\partial V_m^E/\partial T$ for the binary mixtures were calculated. The variations of these parameters with composition and temperature of the mixtures have been discussed in terms of molecular interactions in these mixtures. The V_m^E values were found negative for all the mixtures at each temperature studied, indicating the presence of specific interactions between aniline and alkanol molecules. The extent of negative deviations in V_m^E values follows the order: 1-propanol < 2-propanol < 2-methyl-1-propanol < 2-methyl-2-propanol. It is observed that the V_m^E values depend upon the positions of hydroxyl and methyl groups in these alkanol molecules.

KEY WORDS: alkanols; aniline; density; excess molar volume; molecular interactions.

1. INTRODUCTION

A knowledge of the composition and temperature dependences of the volumetric properties of multicomponent liquid mixtures provides substantial information on the molecular influence on the intensity of the intermolecular interactions among component molecules [1–3]. In previous articles

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[4–11] we have reported studies on volumetric, transport, and acoustic properties of binary mixtures containing alkanols. The present work deals with the volumetric behavior of binary mixtures of aniline with 1-propanol, 2-propanol, 2-methyl-1-propanol, and 2-methyl-2-propanol over the entire composition range at temperatures from 293.15 to 318.15 K. Aniline molecules are polar ($\mu = 1.51$ D at 298.15 K) [12] and self-associated through hydrogen bonding of their amino groups [13], and alkanol molecules are polar and self-associated through hydrogen bonding of their hydroxyl groups [14]. Aniline is used in the manufacture of synthetic dyes, drugs, and as an accelerator in vulcanization of rubber; and the alkanols are of interest in their own right and serve as simple examples of biologically and industrially important amphiphilic materials [15]. Therefore, the study of intermolecular interactions in aniline + alkanol mixtures are particularly interesting because of their industrial applications. A literature survey indicates that there has been no temperature-dependent study of aniline + alkanol mixtures from the point of view of their volumetric behavior, except for the work of Saleh et al. [16]; they studied the volumetric behavior of aniline + 1-propanol mixtures and Nikam et al. [17] studied the volumetric behavior of aniline + *n*-alkanol (C_5–C_{10}) mixtures. These considerations led us to undertake the present study.

In the present article, we report densities, ρ, of binary mixtures of aniline + 1-propanol, 2-propanol, 2-methyl-1-propanol, and 2-methyl-2-propanol, and the pure components at atmospheric pressure and temperatures of 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15 K, covering the entire composition range of the binaries, expressed by the mole fraction, x of aniline. The experimental values of ρ were used to calculate the excess molar volumes, V_m^E, and the temperature coefficients of the excess molar volume, $\partial V_m^E/\partial T$. The variations of these parameters with composition and/or temperature of the mixtures have been discussed in terms of molecular interactions in these mixtures.

2. EXPERIMENTAL

Aniline, 1-propanol, 2-propanol, 2-methyl-1-propanol, and 2-methyl-2-propanol used in the study were products from s. d. fine chemicals, India and were purified by using methods described in the literature [18,19]; the mass fraction purities as determined by gas chromatography are: aniline > 0.996, 1-propanol > 0.996, 2-propanol > 0.995, 2-methyl-1-propanol > 0.995, and 2-methyl-2-propanol > 0.993. Before use, the chemicals were stored over 0.4 nm molecular sieves for 72 h to remove water content, if any, and were degassed at low pressure. The mixtures were prepared by mass and were kept in special airtight stopper glass bottles to avoid

evaporation. The weighings were done on an electronic balance (Model GR-202, AND, Japan) with a precision of ± 0.01 mg. The probable error in the mole fraction was estimated to be less than $\pm 1 \times 10^{-4}$.

The densities of pure liquids and their binary mixtures were measured by using a single-capillary pycnometer (made of Borosil glass) having a bulb capacity of ≈ 10 mL. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using triply distilled water. The densities of pure water at required temperatures were taken from the literature [20]. The reproducibility of density measurements was within $\pm 2 \times 10^{-5}$ g · cm^{-3}. The temperature of the test liquids during the measurements was maintained to an uncertainty of ± 0.01 K in an electronically controlled thermostatted water bath (Model ME-31A, Julabo, Germany). The reliability of the experimental density measurements was demonstrated by comparisons of the experimental data for the pure liquids with values available in the literature [19,21–39] at the studied temperatures. This comparison is given in Table I, and the agreement between the experimental and literature values is, in general, good.

3. RESULTS AND DISCUSSION

The experimental values of densities, ρ, of binary mixtures of aniline with 1-propanol, 2-propanol, 2-methyl-1-propanol, and 2-methyl-2-propanol, with aniline as a common component, over the whole composition range, expressed in mole fraction x of aniline ($0 \leqslant x \leqslant 1$), at temperatures from 293.15 to 318.15 K are listed in Tables II–V. The excess molar volumes V_m^E were calculated by using the following relation,

$$V_m^E = x M_1 (1/\rho - 1/\rho_1) + (1-x) M_2 (1/\rho - 1/\rho_2), \quad (1)$$

where M is the molar mass; subscripts 1 and 2 represent the pure components, aniline and alkanol, respectively. The values of V_m^E calculated by using Eq. (1) are listed in Tables II–V. The variations of V_m^E with mole fraction x of aniline for all four binaries at 298.15 and 318.15 K, along with the smoothed V_m^E values by using the Redlich–Kister equation [40] are presented graphically in Fig. 1.

The results presented in Tables II–V and Fig. 1 indicates that V_m^E values are negative over the entire mole fraction range and at all temperatures investigated for each binary system under study. The observed negative values of V_m^E for aniline + alkanol mixtures indicate the presence of specific interactions between aniline and alkanol molecules. The magnitude of negative V_m^E values follows the sequence: 1-pro-

Table I. Experimental Values of Density, ρ, of Pure Liquids along with Values Available in the Literature at Temperatures from 293.15 to 318.15 K

Liquid	T (K)	ρ(g·cm^{-3})		
		Experimental	Literature	References
Aniline	293.15	1.02171	1.02173	[21]
			1.02170	[19, 22]
	298.15	1.01744	1.01740	[23]
			1.01750	[21]
	303.15	1.01317	–	–
	308.15	1.00890	1.00880	[23]
	313.15	1.00463	–	–
	318.15	1.00036	1.00020	[23]
1-Propanol	293.15	0.80371	0.80362	[24]
			0.80375	[25]
	298.15	0.79974	0.79975	[25]
			0.7996	[19, 24]
	303.15	0.79577	0.79558	[26]
			0.79586	[26]
	308.15	0.79180	0.79185	[25]
			0.7918	[27]
	313.15	0.78783	0.7875	[28]
	318.15	0.78386	0.78359	[25]
2-Propanol	293.15	0.78496	–	–
	298.15	0.78075	0.78056	[29]
	303.15	0.77654	0.77686	[30]
			0.77690	[31]
	308.15	0.77232	0.77220	[31]
	313.15	0.76811	–	–
	318.15	0.76390	–	–
2-Methyl-1-propanol	293.15	0.80148	0.8016	[21]
	298.15	0.79754	0.79737	[32]
			0.79772	[33]
	303.15	0.79360	0.7938	[34]
	308.15	0.78966	0.7897	[35]
	313.15	0.78572	0.7858	[36]
	318.15	0.78178	0.7818	[35]
2-Methyl-2-propanol	293.15	0.78575	–	–
	298.15	0.78063	0.78059	[37]
			0.78068	[33]
	303.15	0.77551	0.77551	[38]
			0.7757	[21]
	308.15	0.77039	0.77019	[32]
	313.15	0.76526	0.76501	[39]
			0.76532	[33]
	318.15	0.76013	–	–

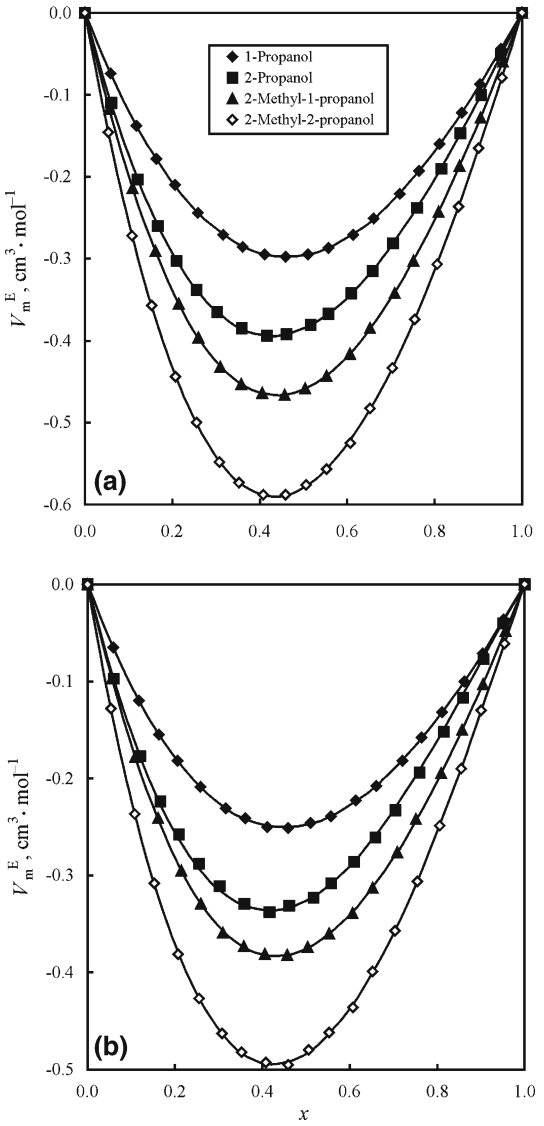

Fig. 1. Variations of excess molar volume, V_m^E, as a function of mole fraction, x, of aniline for aniline + alkanol binary mixtures at (a) 298.15 K and (b) 318.15 K. Points represent experimental values and lines represent smoothed values calculated from Redlich–Kister equation [40].

Table II. Densities, ρ, and Excess Molar Volumes, V_m^E, of Aniline + 1-Propanol Binary Mixtures as a Function of Mole Fraction, x, of Aniline at Temperatures from 293.15 to 318.15 K

x	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)	x	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)
$T = 293.15$ K					
0.0000	0.80371	0.0000	0.5574	0.93905	−0.2975
0.0582	0.81980	−0.0756	0.6141	0.95071	−0.2814
0.1177	0.83575	−0.1421	0.6603	0.95993	−0.2602
0.1628	0.84749	−0.1834	0.7209	0.97173	−0.2288
0.2056	0.85838	−0.2173	0.7646	0.98001	−0.2010
0.2582	0.87143	−0.2518	0.8114	0.98868	−0.1676
0.3156	0.88526	−0.2803	0.8624	0.99790	−0.1266
0.3612	0.89595	−0.2963	0.9041	1.00528	−0.0910
0.4112	0.90736	−0.3058	0.9525	1.01366	−0.0462
0.4585	0.91788	−0.3089	1.0000	1.02171	0.0000
0.5106	0.92918	−0.3068			
$T = 298.15$ K					
0.0000	0.79974	0.0000	0.5574	0.93471	−0.2868
0.0582	0.81577	−0.0737	0.6141	0.94636	−0.2709
0.1177	0.83166	−0.1381	0.6603	0.95559	−0.2514
0.1628	0.84336	−0.1781	0.7209	0.96739	−0.2208
0.2056	0.85421	−0.2105	0.7646	0.97567	−0.1935
0.2582	0.86722	−0.2436	0.8114	0.98434	−0.1604
0.3156	0.88101	−0.2708	0.8624	0.99358	−0.1216
0.3612	0.89167	−0.2857	0.9041	1.00097	−0.0871
0.4112	0.90306	−0.2950	0.9525	1.00937	−0.0443
0.4585	0.91356	−0.2976	1.0000	1.01744	0.0000
0.5106	0.92484	−0.2951			
$T = 303.15$ K					
0.0000	0.79577	0.0000	0.5574	0.93036	−0.2751
0.0582	0.81174	−0.0718	0.6141	0.94199	−0.2584
0.1177	0.82756	−0.1331	0.6603	0.95122	−0.2397
0.1628	0.83922	−0.1717	0.7209	0.96302	−0.2099
0.2056	0.85004	−0.2035	0.7646	0.97131	−0.1840
0.2582	0.86301	−0.2353	0.8114	0.98000	−0.1532
0.3156	0.87676	−0.2611	0.8624	0.98925	−0.1157
0.3612	0.88739	−0.2749	0.9041	0.99666	−0.0832
0.4112	0.89876	−0.2840	0.9525	1.00508	−0.0423
0.4585	0.90924	−0.2862	1.0000	1.01317	0.0000
0.5106	0.92050	−0.2832			

Table II. continued

x	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})	x	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})
$T = 308.15$ K					
0.0000	0.79180	0.0000	0.5574	0.92601	−0.2631
0.0582	0.80770	−0.0689	0.6141	0.93762	−0.2457
0.1177	0.82347	−0.1290	0.6603	0.94685	−0.2278
0.1628	0.83509	−0.1662	0.7209	0.95866	−0.1997
0.2056	0.84587	−0.1963	0.7646	0.96696	−0.1753
0.2582	0.85880	−0.2268	0.8114	0.97567	−0.1467
0.3156	0.87251	−0.2512	0.8624	0.98493	−0.1105
0.3612	0.88311	−0.2639	0.9041	0.99235	−0.0792
0.4112	0.89446	−0.2728	0.9525	1.00079	−0.0404
0.4585	0.90492	−0.2745	1.0000	1.00890	0.0000
0.5106	0.91616	−0.2710			
$T = 313.15$ K					
0.0000	0.78783	0.0000	0.5574	0.92166	−0.2509
0.0582	0.80367	−0.0669	0.6141	0.93326	−0.2338
0.1177	0.81938	−0.1247	0.6603	0.94250	−0.2175
0.1628	0.83096	−0.1606	0.7209	0.95431	−0.1903
0.2056	0.84170	−0.1891	0.7646	0.96261	−0.1664
0.2582	0.85459	−0.2182	0.8114	0.97133	−0.1392
0.3156	0.86826	−0.2411	0.8624	0.98061	−0.1053
0.3612	0.87883	−0.2528	0.9041	0.98804	−0.0751
0.4112	0.89016	−0.2614	0.9525	0.99650	−0.0384
0.4585	0.90060	−0.2627	1.0000	1.00463	0.0000
0.5106	0.91182	−0.2587			
$T = 318.15$ K					
0.0000	0.78386	0.0000	0.5574	0.91732	−0.2395
0.0582	0.79964	−0.0649	0.6141	0.92891	−0.2225
0.1177	0.81529	−0.1204	0.6603	0.93816	−0.2080
0.1628	0.82683	−0.1549	0.7209	0.94997	−0.1817
0.2056	0.83753	−0.1817	0.7646	0.95827	−0.1583
0.2582	0.85038	−0.2094	0.8114	0.96699	−0.1316
0.3156	0.86401	−0.2309	0.8624	0.97629	−0.0999
0.3612	0.87455	−0.2414	0.9041	0.98373	−0.0710
0.4112	0.88586	−0.2499	0.9525	0.99221	−0.0363
0.4585	0.89628	−0.2506	1.0000	1.00036	0.0000
0.5106	0.90748	−0.2462			

Table III. Densities, ρ, and Excess Molar Volumes, V_m^E, of Aniline + 2-Propanol Binary Mixtures as a Function of Mole Fraction, x, of Aniline at Temperatures from 293.15 to 318.15 K

x	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)	x	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)
$T = 293.15$ K					
0.0000	0.78496	0.0000	0.5572	0.93113	−0.3811
0.0595	0.80273	−0.1145	0.6090	0.94269	−0.3556
0.1201	0.82026	−0.2106	0.6580	0.95338	−0.3269
0.1663	0.83323	−0.2688	0.7047	0.96332	−0.2926
0.2094	0.84504	−0.3130	0.7602	0.97488	−0.2481
0.2546	0.85714	−0.3500	0.8149	0.98600	−0.1993
0.3017	0.86943	−0.3776	0.8588	0.99471	−0.1547
0.3582	0.88378	−0.3986	0.9060	1.00391	−0.1053
0.4167	0.89821	−0.4082	0.9512	1.01255	−0.0554
0.4612	0.90889	−0.4065	1.0000	1.02171	0.0000
0.5163	0.92179	−0.3958			
$T = 298.15$ K					
0.0000	0.78075	0.0000	0.5572	0.92662	−0.3667
0.0595	0.79844	−0.1101	0.6090	0.93819	−0.3419
0.1201	0.81591	−0.2033	0.6580	0.94890	−0.3145
0.1663	0.82884	−0.2597	0.7047	0.95886	−0.2815
0.2094	0.84062	−0.3025	0.7602	0.97044	−0.2380
0.2546	0.85269	−0.3381	0.8149	0.98158	−0.1901
0.3017	0.86496	−0.3648	0.8588	0.99032	−0.1473
0.3582	0.87929	−0.3850	0.9060	0.99955	−0.0996
0.4167	0.89371	−0.3944	0.9512	1.00823	−0.0522
0.4612	0.90438	−0.3920	1.0000	1.01744	0.0000
0.5163	0.91728	−0.3815			
$T = 303.15$ K					
0.0000	0.77654	0.0000	0.5572	0.92211	−0.3521
0.0595	0.79416	−0.1066	0.6090	0.93369	−0.3279
0.1201	0.81157	−0.1970	0.6580	0.94442	−0.3020
0.1663	0.82445	−0.2504	0.7047	0.95440	−0.2702
0.2094	0.83620	−0.2918	0.7602	0.96600	−0.2277
0.2546	0.84824	−0.3258	0.8149	0.97716	−0.1807
0.3017	0.86049	−0.3518	0.8588	0.98593	−0.1398
0.3582	0.87480	−0.3711	0.9060	0.99519	−0.0937
0.4167	0.88921	−0.3803	0.9512	1.00391	−0.0489
0.4612	0.89987	−0.3773	1.0000	1.01317	0.0000
0.5163	0.91277	−0.3669			

Table III. continued

x	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})	x	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})
$T = 308.15$ K					
0.0000	0.77232	0.0000	0.5572	0.91761	−0.3386
0.0595	0.78988	−0.1040	0.6090	0.92920	−0.3150
0.1201	0.80722	−0.1904	0.6580	0.93993	−0.2887
0.1663	0.82006	−0.2417	0.7047	0.94993	−0.2582
0.2094	0.83178	−0.2818	0.7602	0.96156	−0.2176
0.2546	0.84379	−0.3142	0.8149	0.97274	−0.1714
0.3017	0.85601	−0.3383	0.8588	0.98154	−0.1323
0.3582	0.87031	−0.3577	0.9060	0.99083	−0.0879
0.4167	0.88471	−0.3666	0.9512	0.99959	−0.0456
0.4612	0.89535	−0.3620	1.0000	1.00890	0.0000
0.5163	0.90827	−0.3535			
$T = 313.15$ K					
0.0000	0.76811	0.0000	0.5572	0.91310	−0.3235
0.0595	0.78560	−0.1004	0.6090	0.92470	−0.3006
0.1201	0.80288	−0.1838	0.6580	0.93544	−0.2748
0.1663	0.81568	−0.2330	0.7047	0.94546	−0.2456
0.2094	0.82735	−0.2697	0.7602	0.95711	−0.2061
0.2546	0.83933	−0.3005	0.8149	0.96832	−0.1617
0.3017	0.85154	−0.3249	0.8588	0.97715	−0.1245
0.3582	0.86582	−0.3433	0.9060	0.98648	−0.0828
0.4167	0.88022	−0.3530	0.9512	0.99528	−0.0431
0.4612	0.89084	−0.3467	1.0000	1.00463	0.0000
0.5163	0.90376	−0.3385			
$T = 318.15$ K					
0.0000	0.76390	0.0000	0.5572	0.90859	−0.3082
0.0595	0.78132	−0.0968	0.6090	0.92020	−0.2860
0.1201	0.79854	−0.1770	0.6580	0.93095	−0.2607
0.1663	0.81130	−0.2242	0.7047	0.94099	−0.2329
0.2094	0.82293	−0.2584	0.7602	0.95266	−0.1944
0.2546	0.83488	−0.2877	0.8149	0.96390	−0.1519
0.3017	0.84707	−0.3112	0.8588	0.97276	−0.1166
0.3582	0.86133	−0.3287	0.9060	0.98212	−0.0767
0.4167	0.87572	−0.3382	0.9512	0.99096	−0.0397
0.4612	0.88633	−0.3313	1.0000	1.00036	0.0000
0.5163	0.89925	−0.3232			

Table IV. Densities, ρ, and Excess Molar Volumes, V_m^E, of Aniline + 2-Methyl-1-propanol Binary Mixtures as a Function of Mole Fraction, x, of Aniline at Temperatures from 293.15 to 318.15 K

x	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)	x	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)
$T = 293.15$ K					
0.0000	0.80148	0.0000	0.5523	0.92700	−0.4631
0.0556	0.81464	−0.1228	0.6061	0.93866	−0.4359
0.1093	0.82724	−0.2231	0.6526	0.94865	−0.4032
0.1610	0.83926	−0.3027	0.7087	0.96066	−0.3588
0.2145	0.85159	−0.3689	0.7512	0.96968	−0.3173
0.2596	0.86189	−0.4117	0.8090	0.98189	−0.2551
0.3099	0.87331	−0.4494	0.8572	0.99199	−0.1954
0.3580	0.88413	−0.4726	0.9051	1.00200	−0.1336
0.4058	0.89479	−0.4841	0.9562	1.01263	−0.0631
0.4573	0.90619	−0.4859	1.0000	1.02171	0.0000
0.5038	0.91641	−0.4787			
$T = 298.15$ K					
0.0000	0.79754	0.0000	0.5523	0.92259	−0.4425
0.0556	0.81062	−0.1178	0.6061	0.93424	−0.4161
0.1093	0.82315	−0.2142	0.6526	0.94423	−0.3846
0.1610	0.83511	−0.2906	0.7087	0.95624	−0.3415
0.2145	0.84739	−0.3547	0.7512	0.96528	−0.3028
0.2596	0.85765	−0.3958	0.8090	0.97751	−0.2434
0.3099	0.86903	−0.4320	0.8572	0.98764	−0.1871
0.3580	0.87981	−0.4534	0.9051	0.99767	−0.1276
0.4058	0.89044	−0.4640	0.9562	1.00833	−0.0602
0.4573	0.90182	−0.4659	1.0000	1.01744	0.0000
0.5038	0.91202	−0.4585			
$T = 303.15$ K					
0.0000	0.79360	0.0000	0.5523	0.91818	−0.4216
0.0556	0.80660	−0.1128	0.6061	0.92982	−0.3959
0.1093	0.81906	−0.2050	0.6526	0.93981	−0.3656
0.1610	0.83096	−0.2782	0.7087	0.95183	−0.3249
0.2145	0.84319	−0.3402	0.7512	0.96088	−0.2880
0.2596	0.85341	−0.3796	0.8090	0.97313	−0.2316
0.3099	0.86475	−0.4143	0.8572	0.98329	−0.1787
0.3580	0.87549	−0.4339	0.9051	0.99334	−0.1215
0.4058	0.88609	−0.4435	0.9562	1.00403	−0.0573
0.4573	0.89745	−0.4456	1.0000	1.01317	0.0000
0.5038	0.90763	−0.4379			

Table IV. continued

x	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})	x	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})
$T = 308.15$ K					
0.0000	0.78966	0.0000	0.5523	0.91377	−0.4004
0.0556	0.80258	−0.1077	0.6061	0.92542	−0.3773
0.1093	0.81497	−0.1957	0.6526	0.93541	−0.3484
0.1610	0.82681	−0.2656	0.7087	0.94743	−0.3090
0.2145	0.83899	−0.3255	0.7512	0.95648	−0.2730
0.2596	0.84917	−0.3631	0.8090	0.96875	−0.2195
0.3099	0.86047	−0.3963	0.8572	0.97893	−0.1692
0.3580	0.87117	−0.4140	0.9051	0.98901	−0.1153
0.4058	0.88174	−0.4227	0.9562	0.99973	−0.0543
0.4573	0.89308	−0.4249	1.0000	1.00890	0.0000
0.5038	0.90324	−0.4169			
$T = 313.15$ K					
0.0000	0.78572	0.0000	0.5523	0.90937	−0.3797
0.0556	0.79856	−0.1025	0.6061	0.92102	−0.3584
0.1093	0.81088	−0.1863	0.6526	0.93101	−0.3308
0.1610	0.82266	−0.2528	0.7087	0.94303	−0.2928
0.2145	0.83479	−0.3104	0.7512	0.95208	−0.2577
0.2596	0.84493	−0.3463	0.8090	0.96437	−0.2072
0.3099	0.85619	−0.3778	0.8572	0.97457	−0.1595
0.3580	0.86685	−0.3937	0.9051	0.98468	−0.1091
0.4058	0.87739	−0.4014	0.9562	0.99543	−0.0513
0.4573	0.88871	−0.4038	1.0000	1.00463	0.0000
0.5038	0.89885	−0.3956			
$T = 318.15$ K					
0.0000	0.78178	0.0000	0.5523	0.90498	−0.3597
0.0556	0.79454	−0.0972	0.6061	0.91662	−0.3392
0.1093	0.80680	−0.1778	0.6526	0.92661	−0.3128
0.1610	0.81852	−0.2409	0.7087	0.93863	−0.2763
0.2145	0.83059	−0.2951	0.7512	0.94768	−0.2421
0.2596	0.84069	−0.3291	0.8090	0.95999	−0.1947
0.3099	0.85191	−0.3591	0.8572	0.97021	−0.1497
0.3580	0.86253	−0.3730	0.9051	0.98035	−0.1027
0.4058	0.87305	−0.3808	0.9562	0.99113	−0.0482
0.4573	0.88434	−0.3822	1.0000	1.00036	0.0000
0.5038	0.89446	−0.3738			

Table V. Densities, ρ, and Excess Molar Volumes, V_m^E, of Aniline + 2-Methyl-2-propanol Binary Mixtures as a Function of Mole Fraction, x, of Aniline at Temperatures from 293.15 to 318.15 K

x	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)	x	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)
$T = 293.15$ K					
0.0000	0.78575	0.0000	0.5532	0.92006	−0.5819
0.0538	0.79932	−0.1510	0.6076	0.93271	−0.5478
0.1082	0.81294	−0.2810	0.6522	0.94296	−0.5053
0.1526	0.82396	−0.3688	0.7028	0.95455	−0.4508
0.2066	0.83730	−0.4605	0.7542	0.96631	−0.3914
0.2552	0.84915	−0.5188	0.8062	0.97812	−0.3207
0.3075	0.86187	−0.5716	0.8544	0.98901	−0.2479
0.3523	0.87264	−0.5983	0.9012	0.99955	−0.1724
0.4074	0.88577	−0.6134	0.9536	1.01132	−0.0833
0.4586	0.89789	−0.6142	1.0000	1.02171	0.0000
0.5064	0.90911	−0.6013			
$T = 298.15$ K					
0.0000	0.78063	0.0000	0.5532	0.91496	−0.5572
0.0538	0.79416	−0.1462	0.6076	0.92768	−0.5250
0.1082	0.80775	−0.2721	0.6522	0.93798	−0.4829
0.1526	0.81875	−0.3567	0.7028	0.94967	−0.4326
0.2066	0.83207	−0.4445	0.7542	0.96150	−0.3741
0.2552	0.84391	−0.4998	0.8062	0.97341	−0.3066
0.3075	0.85661	−0.5479	0.8544	0.98440	−0.2370
0.3523	0.86739	−0.5733	0.9012	0.99504	−0.1645
0.4074	0.88055	−0.5880	0.9536	1.00693	−0.0791
0.4586	0.89270	−0.5882	1.0000	1.01744	0.0000
0.5064	0.90396	−0.5756			
$T = 303.15$ K					
0.0000	0.77551	0.0000	0.5532	0.90987	−0.5333
0.0538	0.78900	−0.1413	0.6076	0.92265	−0.5019
0.1082	0.80256	−0.2630	0.6522	0.93301	−0.4611
0.1526	0.81354	−0.3443	0.7028	0.94479	−0.4142
0.2066	0.82684	−0.4282	0.7542	0.95669	−0.3566
0.2552	0.83868	−0.4816	0.8062	0.96870	−0.2923
0.3075	0.85136	−0.5250	0.8544	0.97979	−0.2259
0.3523	0.86216	−0.5500	0.9012	0.99052	−0.1556
0.4074	0.87535	−0.5644	0.9536	1.00254	−0.0749
0.4586	0.88753	−0.5640	1.0000	1.01317	0.0000
0.5064	0.89882	−0.5506			

Table V. continued

x	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})	x	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})
$T = 308.15$ K					
0.0000	0.77039	0.0000	0.5532	0.90478	−0.5090
0.0538	0.78384	−0.1363	0.6076	0.91763	−0.4796
0.1082	0.79737	−0.2538	0.6522	0.92805	−0.4402
0.1526	0.80833	−0.3317	0.7028	0.93991	−0.3956
0.2066	0.82161	−0.4117	0.7542	0.95188	−0.3389
0.2552	0.83345	−0.4631	0.8062	0.96399	−0.2779
0.3075	0.84612	−0.5028	0.8544	0.97517	−0.2139
0.3523	0.85693	−0.5264	0.9012	0.98600	−0.1467
0.4074	0.87014	−0.5393	0.9536	0.99814	−0.0698
0.4586	0.88237	−0.5405	1.0000	1.00890	0.0000
0.5064	0.89369	−0.5263			
$T = 313.15$ K					
0.0000	0.76526	0.0000	0.5532	0.89969	−0.4850
0.0538	0.77868	−0.1324	0.6076	0.91261	−0.4575
0.1082	0.79218	−0.2455	0.6522	0.92309	−0.4195
0.1526	0.80312	−0.3200	0.7028	0.93502	−0.3763
0.2066	0.81638	−0.3959	0.7542	0.94708	−0.3224
0.2552	0.82822	−0.4452	0.8062	0.95928	−0.2636
0.3075	0.84089	−0.4823	0.8544	0.97055	−0.2019
0.3523	0.85171	−0.5043	0.9012	0.98148	−0.1378
0.4074	0.86494	−0.5158	0.9536	0.99375	−0.0655
0.4586	0.87721	−0.5174	1.0000	1.00463	0.0000
0.5064	0.88857	−0.5034			
$T = 318.15$ K					
0.0000	0.76013	0.0000	0.5532	0.89461	−0.4617
0.0538	0.77352	−0.1284	0.6076	0.90760	−0.4363
0.1082	0.78699	−0.2371	0.6522	0.91813	−0.3986
0.1526	0.79791	−0.3081	0.7028	0.93013	−0.3568
0.2066	0.81116	−0.3811	0.7542	0.94228	−0.3057
0.2552	0.82299	−0.4271	0.8062	0.95457	−0.2492
0.3075	0.83567	−0.4626	0.8544	0.96593	−0.1899
0.3523	0.84649	−0.4820	0.9012	0.97697	−0.1298
0.4074	0.85975	−0.4930	0.9536	0.98936	−0.0613
0.4586	0.87206	−0.4950	1.0000	1.00036	0.0000
0.5064	0.88345	−0.4802			

panol < 2-propanol < 2-methyl-1-propanol < 2-methyl-2-propanol (Tables II–V and Fig.1). This suggests that there is a contraction in volume of the mixtures as we move from 1-propanol to 2-methyl-2-propanol.

A plausible qualitative interpretation of the behavior of these mixtures with composition has been suggested. As stated earlier, the molecules of aniline and alkanol are associated through hydrogen bonding in the pure state [12,13]. Mixing of aniline with alkanols would induce mutual dissociation of the hydrogen-bonded structures present in pure liquids with subsequent formation of (new) H-bonds (H–N···H–O and N–H···O–H) between amino group of aniline and hydroxyl group of alkanol molecules. Equally important is the possibility of formation of weak hydrogen bonding ($\pi \cdots\cdots$H–O) involving π-electrons of the benzene ring of aniline and hydroxyl group of alkanols apart from hydrogen bonding between unlike molecules, leading to a contraction in volume, which results in negative V_m^E values.

Furthermore, the magnitude of negative V_m^E values (Fig. 1) at equimolar composition of these mixtures at 298.15 K follows the order: 1-propanol < 2-propanol < 2-methyl-1-propanol < 2-methyl-2-propanol, which, in turn, indicates the order of the interactions between aniline and alkanol molecules in these mixtures. The more negative V_m^E values for aniline + 2-propanol than those for aniline + 1-propanol (Fig. 1), are due to the fact that in 2-propanol the presence of two $-CH_3$ group at the α-carbon atom increase the electron density at the oxygen atom to a greater extent than that in 1-propanol which has one ethyl group on the α-carbon atom, resulting in stronger interaction (H-bonding) in the aniline + 2-propanol mixtures. Also, the more negative V_m^E values for aniline + 2-methyl-2-propanol than those for aniline + 2-methyl-1-propanol (Fig. 1), are due to the fact that in 2-methyl-2-propanol the presence of three $-CH_3$ groups on the α-carbon atom increase the electron density at the oxygen atom to a greater extent than that in 2-methyl-1-propanol which has two $-CH_3$ groups at the β-carbon, resulting in stronger interaction (H-bonding) in the aniline + 2-methyl-2-propanol mixtures. Hence, it may be concluded that the interaction between aniline and alkanols under study increases when a hydroxyl group is attached to a carbon atom with a greater number of $-CH_3$ groups, i.e., an increase in the number of $-CH_3$ groups at the α-carbon atom of alkanols.

The values of V_m^E increase with an increase in temperature of the mixture (Tables II–V and Fig. 1) for all the four systems under study. The increase in V_m^E is attributed to the decrease in the magnitude of solute–solvent interactions with a rise in temperature, leading to an expansion in volume, hence, resulting in an increase in V_m^E values. Furthermore, the

Table VI. Temperature Coefficients of the Excess Molar Volume, $\partial V_m^E/\partial T(10^{-3}cm^3 \cdot mol^{-1} \cdot K^{-1})$ as a Function of Mole Fraction, x, of Aniline for Aniline + Alkanol Binary Mixtures

x Aniline + 1-Propanol	$\partial V_m^E/\partial T$	x Aniline + 1-Propanol	$\partial V_m^E/\partial T$	x Aniline + 2-Methyl-1-propanol	$\partial V_m^E/\partial T$	x Aniline + 2-Methyl-2-propanol	$\partial V_m^E/\partial T$
0.0582	0.440	0.0595	0.687	0.0556	1.023	0.0538	0.910
0.1177	0.871	0.1201	1.330	0.1093	1.825	0.1082	1.765
0.1628	1.143	0.1663	1.780	0.1610	2.485	0.1526	2.435
0.2056	1.428	0.2094	2.179	0.2145	2.954	0.2066	3.195
0.2582	1.698	0.2546	2.493	0.2596	3.303	0.2552	3.660
0.3156	1.975	0.3017	2.657	0.3099	3.615	0.3075	4.365
0.3612	2.197	0.3582	2.786	0.3580	3.985	0.3523	4.641
0.4112	2.238	0.4167	2.790	0.4058	4.141	0.4074	4.823
0.4585	2.329	0.4612	3.012	0.4573	4.144	0.4586	4.754
0.5106	2.425	0.5163	2.886	0.5038	4.194	0.5064	4.838
0.5574	2.343	0.5572	2.901	0.5523	4.152	0.5532	4.812
0.6141	2.391	0.6090	2.770	0.6061	3.860	0.6076	4.472
0.6603	2.142	0.6580	2.647	0.6526	3.603	0.6522	4.257
0.7209	1.924	0.7047	2.388	0.7087	3.283	0.7028	3.754
0.7646	1.735	0.7602	2.136	0.7512	3.007	0.7542	3.439
0.8114	1.426	0.8149	1.894	0.8090	2.418	0.8062	2.862
0.8624	1.073	0.8588	1.522	0.8572	1.835	0.8544	2.328
0.9041	0.800	0.9060	1.140	0.9051	1.236	0.9012	1.729
0.9525	0.393	0.9512	0.624	0.9562	0.598	0.9536	0.891

temperature coefficients of the excess molar volume, $\partial V_m^E/\partial T$ at each mole fraction have also been calculated and are listed in Table VI. A perusal of Table VI reveals that $\partial V_m^E/\partial T$ values are positive for all the four systems under study, indicating that there is a decrease in the magnitude of interactions between aniline and alkanol molecules in these mixtures, which results in an expansion in volume with a rise in temperature. Thus, the behaviors of V_m^E and $\partial V_m^E/\partial T$ are consistent with each other.

ACKNOWLEDGMENTS

The author is thankful to Department of Science and Technology (DST), New Delhi, India for financial support in the form of SERC Fast Track Young Scientist Scheme. The author is also thankful to Dr. I. S. Bakshi, Principal, Dyal Singh College (University of Delhi), New Delhi for encouragement and providing facilities.

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