J. Chem. Eng. Data **2008,** *53,* 857–862 **857**

Densities, Excess Molar Volumes, Speeds of Sound at (293.15, 298.15, and 303.15) K and Isentropic Compressibilities at 298.15 K for 1-Butanol, 1-Pentanol, or 1-Hexanol + Dibutylether Systems

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Densities, ρ, and speeds of sound, u, of systems formed by 1-butanol (1-BuOH), 1-pentanol (1-PeOH), or 1-HxOH (1-hexanol) and dibutylether (DBE) have been measured at (293.15, 298.15, and 303.15) K and atmospheric pressure using a vibrating-tube densimeter and sound analyzer Anton Paar model DSA-5000. The ρ and u values were used to calculate excess molar volumes, V^E, and deviations from the ideal behavior of the thermal expansion coefficient, α_P, and of the isentropic compressibilities, κ_T. The V^E variation with the chain length of the 1-alkanol shows the existence of structural effects for systems including longer 1-alkanols.

1. Introduction

Oxygenated compounds are important substances from a practical point of view, as they are increasingly used as additives to gasoline due to their octane-enhancing and pollution-reducing properties.[1,2] From a theoretical point of view, systems involving oxaalkanes are of high interest because they make it possible to study the influence of a number of effects (e.g., steric or proximity effects, cyclization) on the interactions present in the mixture considered. 1-Alkanol + oxaalkane mixtures are particularly interesting due to their complexity which is consequence of the self-association of the alkanols partially destroyed by the active molecules of ethers and of the new intermolecular OH−O bonds created. So, the treatment of this class of systems is a severe test for any theoretical model. Moreover, the analysis of the present systems is a previous step to the study of mixtures containing hydroxyethers, where the intramolecular effects between the −OH and −O− groups in the same cellosolve molecule become of great importance.[3]

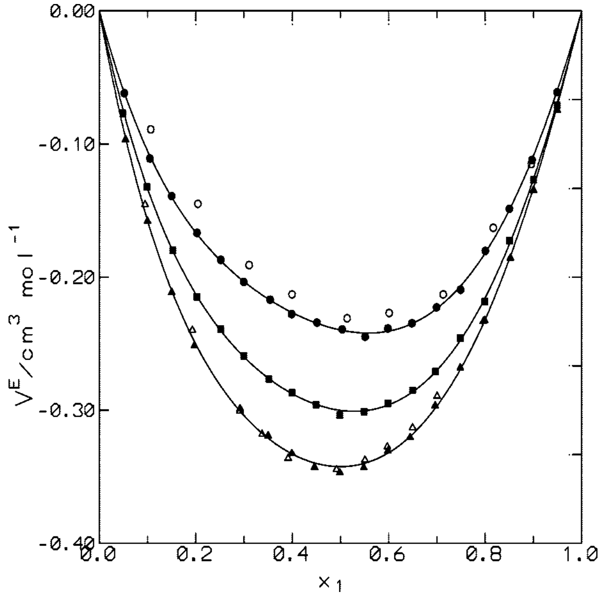

Figure 1. V^E at 298.15 K for 1-alkanol (1) + dibutylether (2) mixtures. Solid lines, calculations with eq 6 using the coefficients from Table 4. Points, experimental results: •, 1-butanol; ■, 1-pentanol; ▲, 1-hexanol (this work); ○, 1-butanol;[11] △, 1-hexanol.[6]

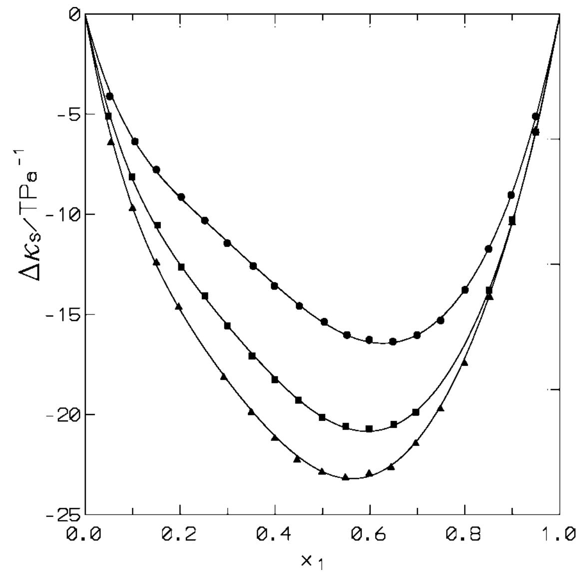

Figure 2. $\Delta\kappa_S$ at 298.15 K for 1-alkanol (1) + dibutylether (2) mixtures. Solid lines, calculations with eq 6 using the coefficients from Table 4. Points, experimental results (this work): •, 1-butanol; ■, 1-pentanol; ▲, 1-hexanol.

As a continuation of our previous experimental studies on alkanol + ether systems,[4–10] in this paper, ρ, u, and related quantities such as V^E, $\Delta\alpha_P$, and $\Delta\kappa_S$ are reported for systems formed by 1-BuOH, or 1-PeOH, or 1-HxOH and DBE. V^E data at 298.15 K are available in the literature for the systems with 1-BuOH[11] or 1-HxOH.[6]

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10.1021/je7005727 CCC: $40.75

Table 1. Physical Properties of Pure Compounds, 1-Butanol (1-BuOH), 1-Pentanol (1-PeOH), 1-Hexanol (1-HxOH), and Dibutylether (DBE) at Temperature T: ρ, Density; u, Speed of Sound; α_p, Isobaric Thermal Expansion Coefficient; κ_S, Adiabatic Compressibility; κ_T, Isothermal Compressibility; C_v, Isochoric Heat Capacity; and C_p, Isobaric Heat Capacity

		1-BuOH		1-PeOH		1-HxOH		DBE	
property	T/K	exptl	lit.	exptl	lit.	exptl	lit.	exptl	lit.
$\rho/\mathrm{g\cdot cm^3}$	293.15	0.809644	0.8095[a] 0.80956[b]	0.814738	0.81445[b]	0.818962	0.81875[b]	0.768468	0.76884[c]
	298.15	0.805842	0.80575[a]	0.811067	0.81080[b]	0.815387	0.81534[b]	0.764170	0.76411[c]
	303.15	0.801995	0.8018[a] 0.80194[d]	0.807366	0.80736[d] 0.80739[f]	0.811783	0.81172[e]	0.759829	0.76017[c] 0.75973[g]
$u/\mathrm{m\cdot s^{-1}}$	293.15	1256.74	1257[a]	1292.52		1320.32		1181.82	
	298.15	1239.19	1240[a]	1275.08	1277.2[h]	1303.03	1303[i]	1161.19	1161.6[j]
	303.15	1222.70		1258.46	1258.2[f]	1286.34	1285.6[e]	1142.07	
$\alpha_p/10^{-3}\mathrm{K^{-1}}$	298.15	0.9493	0.948[b]	0.9090	0.905[b]	0.8805	0.878[b]	1.1307	1.1335[c]
$\kappa_s/\mathrm{TPa^{-1}}$	293.15	782.01		734.69		700.45		931.69	
	298.15	808.12	807[a]	758.35		722.31	722[i]	970.52	
	303.15	834.04		782.08	782[f]	744.47		1009.02	
$\kappa_T/\mathrm{TPa^{-1}}$	298.15	949.24	942[b]	886.48	884[b]	842.34	824[b]	1204.03	
$C_p/\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	298.15		175.14[k]		208.98[l]		241.32[m]		278.2[n]
$C_v/\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	298.15	149.1		178.8		206.9		224.2	

[a] Ref 26. [b] Ref 13. [c] Ref 27. [d] Ref 28. [e] Ref 29. [f] Ref 30. [g] Ref 31. [h] Ref 32. [i] Ref 33. [j] Ref 34. [k] Ref 35. [l] Ref 36. [m] Ref 37. [n] Ref 38.

Table 2. Densities, ρ, Molar Excess Volumes, V^E, and Deviations from the Ideal Behavior of the Speed of Sound, Δu, for 1-Alkanol (1) + 1-Dibutylether (2) Mixtures at Temperature T

	ρ	V^E	Δu		ρ	V^E	Δu
x_1	$\mathrm{g\cdot cm^{-3}}$	$\mathrm{cm^3\cdot mol^{-1}}$	$\mathrm{m\cdot s^{-1}}$	x_1	$\mathrm{g\cdot cm^{-3}}$	$\mathrm{cm^3\cdot mol^{-1}}$	$\mathrm{m\cdot s^{-1}}$
1-Butanol (1) + Dibutylether (2); T = 293.15 K							
0.0547	0.770042	−0.0700	−1.046	0.5008	0.784403	−0.2432	−12.296
0.1046	0.771461	−0.1144	−2.817	0.5997	0.788444	−0.2424	−12.117
0.1516	0.772810	−0.1464	−4.631	0.6500	0.790668	−0.2373	−11.553
0.2005	0.774247	−0.1719	−6.421	0.6984	0.792900	−0.2245	−10.792
0.2514	0.775785	−0.1921	−8.065	0.7464	0.795233	−0.2083	−9.727
0.3016	0.777369	−0.2089	−9.427	0.8488	0.800592	−0.1493	−6.633
0.3518	0.779033	−0.2238	−10.517	0.8980	0.803384	−0.1107	−4.714
0.4012	0.780726	−0.2329	−11.368	0.9493	0.806449	−0.0605	−2.433
0.4519	0.782556	−0.2398	−11.934				
1-Butanol (1) + Dibutylether (2); T = 298.15 K							
0.0517	0.765646	−0.0618	−0.981	0.5514	0.782295	−0.2448	−12.766
0.1047	0.767168	−0.1109	−2.909	0.5983	0.784258	−0.2386	−12.599
0.1499	0.768464	−0.1391	−4.650	0.6481	0.786487	−0.2347	−12.079
0.2024	0.770022	−0.1668	−6.605	0.6993	0.788884	−0.2227	−11.233
0.2519	0.771537	−0.1871	−8.255	0.7489	0.791361	−0.2095	−10.079
0.2992	0.773045	−0.2036	−9.597	0.8004	0.794002	−0.1804	−8.640
0.3540	0.774860	−0.2170	−10.923	0.8501	0.796724	−0.1487	−6.889
0.3987	0.776425	−0.2278	−11.700	0.8974	0.799453	−0.1119	−4.956
0.4511	0.778326	−0.2342	−12.359	0.9492	0.802596	−0.0611	−2.543
0.5037	0.780345	−0.2392	−12.748				
1-Butanol (1) + Dibutylether (2); T = 303.15 K							
0.0544	0.761363	−0.0585	−1.138	0.5493	0.777978	−0.2352	−13.280
0.1019	0.762717	−0.0982	−2.835	0.6069	0.780477	−0.2360	−12.997
0.1509	0.764148	−0.1320	−4.793	0.6491	0.782394	−0.2314	−12.537
0.2038	0.765743	−0.1621	−6.779	0.7005	0.784812	−0.2170	−11.695
0.2505	0.767184	−0.1811	−8.395	0.7451	0.787095	−0.2102	−10.555
0.3025	0.768842	−0.1959	−9.942	0.8001	0.789991	−0.1843	−8.908
0.3542	0.770576	−0.2088	−11.238	0.8482	0.792622	−0.1496	−7.242
0.3972	0.772093	−0.2192	−12.062	0.8990	0.795603	−0.1106	−5.083
0.4501	0.774032	−0.2265	−12.807	0.9494	0.798700	−0.0605	−2.690
0.5002	0.775970	−0.2315	−13.188				
1-Pentanol (1) + Dibutylether (2); T = 293.15 K							
0.0993	0.772147	−0.1349	−3.015	0.5527	0.790629	−0.3015	−13.687
0.1509	0.774059	−0.1813	−5.244	0.5997	0.792852	−0.2949	−13.418
0.1989	0.775841	−0.2114	−7.193	0.6510	0.795356	−0.2828	−12.764
0.2498	0.777791	−0.2399	−9.011	0.6975	0.797695	−0.2662	−11.904
0.2983	0.779683	−0.2594	−10.535	0.7501	0.800433	−0.2411	−10.599
0.3468	0.781629	−0.2748	−11.731	0.7985	0.803030	−0.2097	−9.137
0.3961	0.783670	−0.2859	−12.663	0.8506	0.805928	−0.1707	−7.182
0.4504	0.785990	−0.2943	−13.328	0.9000	0.808751	−0.1233	−5.067

Table 2 Continued

x_1	ρ / $\mathrm{g \cdot cm^{-3}}$	V^E / $\mathrm{cm^3 \cdot mol^{-1}}$	Δu / $\mathrm{m \cdot s^{-1}}$	x_1	ρ / $\mathrm{g \cdot cm^{-3}}$	V^E / $\mathrm{cm^3 \cdot mol^{-1}}$	Δu / $\mathrm{m \cdot s^{-1}}$
1-Pentanol (1) + Dibutylether (2); $T = 298.15$ K							
0.4987	0.788132	−0.2983	−13.744	0.9491	0.811645	−0.0679	−2.666
0.0486	0.766003	−0.0770	−0.988	0.5487	0.786388	−0.3015	−14.082
0.0986	0.767846	−0.1321	−2.983	0.5982	0.788753	−0.2949	−13.838
0.1521	0.769844	−0.1799	−5.299	0.6496	0.791307	−0.2850	−13.202
0.2022	0.771744	−0.2148	−7.238	0.6966	0.793726	−0.2709	−12.283
0.2520	0.773657	−0.2391	−9.199	0.7484	0.796453	−0.2458	−10.982
0.2996	0.775544	−0.2591	−10.694	0.7990	0.799243	−0.2184	−9.324
0.3515	0.777661	−0.2763	−11.996	0.8506	0.802115	−0.1726	−7.408
0.3997	0.779682	−0.2870	−12.961	0.9002	0.805013	−0.1268	−5.199
0.4497	0.781857	−0.2958	−13.657	0.9490	0.807933	−0.0711	−2.717
0.4986	0.784078	−0.3038	−13.992				
1-Pentanol (1) + Dibutylether (2); $T = 303.15$ K							
0.0495	0.761694	−0.0751	−1.077	0.5493	0.782353	−0.3063	−14.301
0.1034	0.763696	−0.1328	−3.228	0.6003	0.784842	−0.3022	−13.983
0.1526	0.765548	−0.1750	−5.394	0.6499	0.787293	−0.2846	−13.464
0.2049	0.767554	−0.2108	−7.584	0.6988	0.789821	−0.2659	−12.585
0.2523	0.769408	−0.2363	−9.264	0.7492	0.792539	−0.2438	−11.257
0.2985	0.771264	−0.2572	−10.776	0.8001	0.795362	−0.2121	−9.589
0.3486	0.773336	−0.2750	−12.138	0.8510	0.798284	−0.1727	−7.596
0.3990	0.775471	−0.2860	−13.123	0.8974	0.801027	−0.1288	−5.490
0.4497	0.777705	−0.2956	−13.811	0.9493	0.804201	−0.0713	−2.775
0.4978	0.779891	−0.2996	−14.318				
1-Hexanol (1) + Dibutylether (2); $T = 293.15$ K							
0.1135	0.773646	−0.1760	−3.300	0.5487	0.794145	−0.3338	−12.851
0.1548	0.775499	−0.2163	−5.036	0.6000	0.796770	−0.3231	−12.499
0.1968	0.777383	−0.2479	−6.684	0.6466	0.799236	−0.3141	−11.767
0.2469	0.779653	−0.2776	−8.435	0.6987	0.802000	−0.2911	−10.914
0.2969	0.781940	−0.2991	−9.909	0.7487	0.804703	−0.2624	−9.718
0.3470	0.784277	−0.3161	−11.040	0.8001	0.807530	−0.2253	−8.210
0.4017	0.786883	−0.3294	−11.949	0.8478	0.810199	−0.1850	−6.605
0.4491	0.789183	−0.3364	−12.491	0.8994	0.813126	−0.1309	−4.588
0.4976	0.791595	−0.3411	−12.842	0.9500	0.816052	−0.0716	−2.327
1-Hexanol (1) + Dibutylether (2); $T = 298.15$ K							
0.0541	0.766673	−0.0958	−1.002	0.5482	0.790177	−0.3424	−13.019
0.0997	0.768754	−0.1571	−2.740	0.5981	0.792753	−0.3300	−12.771
0.1500	0.771046	−0.2107	−4.847	0.6444	0.795225	−0.3197	−12.097
0.1969	0.773192	−0.2508	−6.651	0.6961	0.798006	−0.2960	−11.237
0.2918	0.777553	−0.2982	−9.814	0.7483	0.800877	−0.2674	−9.996
0.3499	0.780298	−0.3185	−11.260	0.7990	0.803718	−0.2317	−8.438
0.3992	0.782683	−0.3318	−12.115	0.8524	0.806753	−0.1849	−6.578
0.4465	0.785027	−0.3423	−12.622	0.9000	0.809499	−0.1342	−4.697
0.4986	0.787645	−0.3463	−13.010	0.9492	0.812385	−0.0737	−2.466
1-Hexanol (1) + Dibutylether (2); $T = 303.15$ K							
0.0543	0.762348	−0.0926	−1.009	0.5501	0.786255	−0.3437	−13.167
0.0990	0.764409	−0.1533	−2.656	0.5984	0.788815	−0.3363	−12.842
0.2007	0.769103	−0.2503	−6.763	0.6564	0.791951	−0.3196	−12.122
0.2510	0.771443	−0.2808	−8.525	0.6982	0.794233	−0.2985	−11.348
0.3035	0.773930	0.3071	−10.119	0.7491	0.797128	−0.2791	−10.111
0.3511	0.776214	−0.3225	−11.294	0.7991	0.799914	−0.2334	−8.611
0.3985	0.778537	−0.3351	−12.113	0.8490	0.802800	−0.1891	−6.846
0.4482	0.781018	−0.3432	−12.711	0.8961	0.805567	−0.1406	−4.913
0.4989	0.783601	−0.3471	−13.161	0.9505	0.808803	−0.0724	−2.488

2. Experimental

2.1. Materials. 1-Butanol and DBE (puriss p.a., ≥ 99.5 %), 1-pentanol (puriss p.a., ≥ 99 %), 1-hexanol (puriss, ≥ 99 %) were from Fluka and were used without further purification. The ρ and u values of the pure liquids are in good agreement with those from the literature (Table 1). The water contents were determined by the Karl Fischer method as being (0.074, 0.169, 0.186, and 0.006) mol % for 1-butanol, 1-pentanol, 1-hexanol, and DBE, respectively.

2.2. Apparatus and Procedure. Binary mixtures were prepared by mass in small vessels of about 10 cm^3. Caution was taken to prevent evaporation, and the error in the final mole fraction is estimated to be less than ± 0.0001. Conversion to molar quantities was based on the relative atomic mass table of 1985 issued by I.U.P.A.C.[12]

The densities and speeds of sound of both pure liquids and the mixtures were measured using a vibrating-tube densimeter and a sound analyzer (Anton Paar model DSA-5000) automatically thermostatted within ± 0.01 K. The calibration of the apparatus was carried out with deionized double-distilled water, hexane, heptane, octane, isooctane, cyclohexane, and benzene, using ρ values from the literature.[13–15] The accuracy for the ρ and u measurements is $\pm\ 1 \cdot 10^{-2}\ \mathrm{kg \cdot m^{-3}}$ and $\pm\ 0.1\ \mathrm{m \cdot s^{-1}}$, respectively, and the corresponding precisions are $\pm\ 1 \cdot 10^{-3}$

Table 3. Deviations from the Ideal Behavior at 298.15 K for κ_S, Isentropic Compressibility, and α_p, Isobaric Thermal Expansion Coefficient for 1-Alkanol (1) + Dibutylether (2) Mixtures

x_1	$\Delta\kappa_S$ / TPa^{-1}	$\Delta\alpha_P$ / $10^{-6}\ \mathrm{K}^{-1}$
1-Butanol (1) + Dibutylether (2)		
0.0517	−4.11	4.8
0.1047	−6.37	7.9
0.1499	−7.77	9.6
0.2024	−9.13	10.6
0.2519	−10.31	11.0
0.2992	−11.44	11.1
0.3540	−12.58	11.0
0.3987	−13.58	10.8
0.4511	−14.58	10.4
0.5037	−15.37	9.9
0.5514	−16.02	9.3
0.5983	−16.27	8.5
0.6481	−16.36	7.4
0.6993	−16.03	5.9
0.7489	−15.30	4.1
0.8004	−13.78	2.1
0.8501	−11.73	0.2
0.8974	−9.04	−1.2
0.9492	−5.11	−1.6
1-Pentanol (1) + Dibutylether (2)		
0.0486	−5.10	2.9
0.0986	−8.14	4.4
0.1521	−10.54	4.9
0.2022	−12.62	4.7
0.2520	−14.08	4.1
0.2996	−15.56	3.4
0.3515	−17.08	2.5
0.3997	−18.25	1.8
0.4497	−19.28	1.1
0.4986	−20.14	0.7
0.5487	−20.59	0.3
0.5982	−20.71	0.0
0.6496	−20.49	−0.2
0.6966	−19.88	−0.4
0.7484	−18.56	−0.7
0.7990	−16.69	−0.9
0.8506	−13.79	−1.1
0.9002	−10.26	−1.1
0.9490	−5.90	−0.9
1-Hexanol (1) + Dibutylether (2)		
0.0541	−6.37	2.7
0.0997	−9.66	3.6
0.1500	−12.37	3.4
0.1969	−14.59	2.6
0.2918	−18.10	0.2
0.3499	−19.84	−1.3
0.3992	−21.15	−2.4
0.4465	−22.21	−3.2
0.4986	−22.83	−3.9
0.5482	−23.11	−4.3
0.5981	−22.91	−4.5
0.6444	−22.59	−4.6
0.6961	−21.40	−4.6
0.7483	−19.68	−4.5
0.7990	−17.39	−4.4
0.8524	−14.10	−4.0
0.9000	−10.37	−3.4
0.9492	−5.77	−2.2

$\mathrm{kg \cdot m^{-3}}$ and ± 0.01 $\mathrm{m \cdot s^{-1}}$. The experimental technique was checked by determining V^E and u of the standard mixtures (cyclohexane + benzene) at the temperatures (293.15, 298.15, and 303.15) K and cyclohexane + hexane and 2-ethoxyethanol + heptane at 298.15 K. Our results agree well with published values.[16–19] The accuracy in V^E is believed to be less than $\pm(0.01|V^E_{\max}| + 0.005\ \mathrm{cm^3 \cdot mol^{-1}})$, where $|V^E_{\max}|$ denotes the maximum experimental value of the excess molar volume with respect to the mole fraction. The accuracy of the deviations of u from the ideal behavior is estimated to be 0.3 $\mathrm{m \cdot s^{-1}}$.

3. Equations

The thermodynamic properties for which values are derived most directly from the experimental measurements are the density, ρ, the molar volume, V, the coefficient of thermal expansion, $\alpha_P = -1/\rho(\partial\rho/\partial T)_P$ and the isentropic compressibility, κ_S. In this work, α_P values were obtained from a linear dependence of ρ with T. Assuming that the absorption of the acoustic wave is negligible, κ_S can be calculated using the Newton−Laplace equation

$$\kappa_S = \frac{1}{\rho u^2} \tag{1}$$

For an ideal mixture at the same temperature and pressure as the system under study, the values M^{id} of the thermodynamic property, M, are calculated using the equations[16,20]

$$M^{\mathrm{id}} = x_1 M_1 + x_2 M_2 \quad (M = V;\, u,\, C_p) \tag{2}$$

and

$$M^{\mathrm{id}} = \varphi_1 M_1 + \varphi_2 M_2 \quad (M = \alpha_P;\, \kappa_T) \tag{3}$$

where C_P is the isobaric heat capacity; $\varphi_i = x_i V_i / V^{\mathrm{id}}$ is the volume fraction; and M_i is the M value of component i, respectively. For κ_S, the ideal values are calculated according to:

$$\kappa_S = \kappa_T - \frac{TV\alpha_P^2}{C_P} \tag{4}$$

In this article, we have determined the deviations

$$\Delta M = M - M^{\mathrm{id}} \tag{5}$$

Obviously, $\Delta M = M^E$ (excess function) when M is an intensive function (V).

4. Results and Discussion

Table 2 lists values of densities, calculated V^E and of Δu vs x_1, the mole fraction of the 1-alkanol. Table 3 contains the derived quantities $\Delta\kappa_S$ and $\Delta\alpha_P$. The data were fitted by unweighted least-squares polynomial regression to the equation

$$\Delta M = x_1(1 - x_1)\sum_{i=0}^{k-1} A_i(2x_1 - 1)^i \tag{6}$$

where M stands for the properties cited above. The number of coefficients k used in eq 6 for each mixture was determined by applying an F-test[21] at the 99.5 % confidence level. Table 4 lists the parameters A_i obtained in the regression, together with the standard deviations σ, defined by

$$\sigma(\Delta M) = \left[\frac{1}{N-k}\sum(\Delta M_{\mathrm{calcd}} - \Delta M_{\mathrm{exptl}})^2\right]^{1/2} \tag{7}$$

where N is the number of direct experimental values. Results on V^E and $\Delta\kappa_S$ are shown graphically in Figures 1 and 2. V^E data at 298.15 K for the systems with 1-BuOH or 1-HxOH are in agreement with those available in the literature[6,11] (Figure 1).

Hereafeter, we are referring to values of the excess properties at equimolar composition and 298.15 K. V^E of 1-alkanol + DBE mixtures is the result of different contributions. So, the disruption, upon mixing, of the alkanol−alkanol and DBE−DBE

Table 4. Coefficients A_i and Standard Deviations, $\sigma(\Delta M)$ (Equation 7), for Representation of ΔM^a at Temperature T for 1-Alkanol (1) + Dibutylether (2) Systems by Equation 6

system[b]	T/K	property (ΔM)	A_0	A_1	A_2	A_3	A_4	$\sigma(M)$
1-BuOH + DBE	293.15	V^E	−0.974	−0.127	−0.373	0.218		0.0012
		Δu	−48.93	−6.3	2.6	−11.3	17	0.06
	298.15	V^E	−0.959	−0.152	−0.362	0.20		0.0015
		Δu	−50.80	−7.6	4.2	−10.9	15.5	0.06
		$\Delta \kappa_S$	−61.50	−30.6	−19.1	18.5	−25	0.10
		$\Delta \alpha_P$	39.84	−21.01	6.6	−64.2	−19.9	0.02
	303.15	V^E	−0.932	−0.172	−0.360	0.14		0.002
		Δu	−52.73	−8.7	6.8	−10.7	12.4	0.06
1-PeOH + DBE	293.15	V^E	−1.196	−0.077	−0.362	0.26		0.0014
		Δu	−54.73	−5.8	6.0	−11.7	13.5	0.05
	298.15	V^E>	−1.201	−0.096	−0.382	0.23		0.0018
		Δu	−56.03	−7.1	6.2	−12.0	16	0.07
		$\Delta \kappa_S$	−80.5	−28.6	−18	22	−28	0.13
		$\Delta \kappa_S$>	2.78	−17.2	25.0	−33.6		0.05
	303.15	V^E>	−1.205	−0.102	−0.32	0.21		0.003
		Δu	−56.88	−8.1	4.5	−11.5	18	0.07
1-HxOH + DBE	293.15	V^E	−1.348	0.024	−0.399	0.27		0.0019
		Δu	−51.22	−3.5	7.7	−12.1	12	0.07
	298.15	V^E	−1.370		−0.381	0.270		0.002
		Δu	−51.98	−4.3	6.4	−13.8	16	0.08
		$\Delta \kappa_S$	−91.4	−21.8	−13	26	−29	0.13
		$\Delta \kappa_S$>	−15.42	−20.1	26.4	−44.1		0.05
	303.15	V^E	−1.385		−0.354	0.201		0.002
		Δu	−52.42	−5.4	7.4	−13.9	16	0.07

[a] $\Delta M = V^E$, units, $cm^3 \cdot mol^{-1}$; $\Delta M = \Delta u$, units, $m \cdot s^{-1}$; $\Delta M = \Delta \kappa_S$, units, TPa^{-1}; $\Delta M = \Delta \alpha_P$, units, 10^{-6} K^{-1}. [b] For symbols, see Table 1.

interactions contributes positively to H^E, while a negative contribution comes from the creation of the new alcohol−DBE interactions. The former contributions are more important as H^E is positive. In addition, for a fixed alcohol, say 1-propanol, $H^E(\text{DBE})^{22} = 846 > H^E(\text{octane})^{23} = 684$ J·mol^{-1}, which reveals that the main contribution to H^E is due to the breaking of the alkanol−alkanol interactions by the more active DBE molecules. This is supported by the H^E variation, similar for 1-alkanol + DBE, or + fixed alkane mixtures. In the case of DBE systems:[22] $H^E(\text{methanol}) = 802 < H^E(\text{ethanol}) = 858 > H^E(\text{1-propanol}) = 846 > H^E(\text{1-heptanol}) = 773$ (all values in J·mol^{-1}).

V^E is also the result of different contributions. The interactional one is similar to that of H^E. The so-called structural contribution, free volume effects, and interstitial accommodation lead to decreased V^E values.[24] For 1-alkanol + fixed alkane (e.g, heptane) mixtures, V^E is positive for lower 1-alkanols and negative for longer 1-alcohols, which has been typically attributed to the interstitial accommodation of the alkane in the more open network of the longer alkanols.[24] For the actual systems, V^E varies similarly (values in cm^3·mol^{-1}): $V^E(\text{methanol})^{25} = -0.1695 < V^E(\text{ethanol})^{25} = -0.0972 > V^E(\text{1-propanol})^{6} = -0.1846 > V^E(\text{1-butanol}) = -0.2397 > V^E(\text{1-pentanol}) = -0.3002 > V^E(\text{1-hexanol}) = -0.3425$ (this work), which points out the existence of structural effects for those mixtures containing longer 1-alkanols. The negative V^E values for systems with the shorter 1-alkanols may be ascribed to interaction between unlike molecules which are stronger in the methanol system.

5. Conclusions

Densities and speeds of sound of systems formed by 1-butanol, 1-pentanol, or 1.hexanol and DBE have been measured at (293.15, 298.15, and 303.15) K and atmospheric pressure. The ρ and u values were used to calculate V^E at the same temperatures and $\Delta \alpha_P$ and $\Delta \kappa_S$ at 298.15 K. The V^E variation with the chain length of the 1-alkanol shows the existence of structural effects for systems including longer 1-alkanols. Negative V^E values of mixtures with the shorter 1-alkanols can be ascribed to interactions between unlike molecules.

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Received for review October 4, 2007. Accepted November 8, 2007. The authors gratefully acknowledge the financial support received from the Consejería de Educación y Cultura of Junta de Castilla y León, under Projects VA080A06 and VA075A07, and from the Ministerio de Educación y Ciencia, under the Project FIS2007-61833.

JE7005727