J Therm Anal Calorim (2010) 100:707–715
DOI 10.1007/s10973-009-0157-6

Densities and excess molar volumes for mixtures of methanol with other alcohols at temperatures (288.15–313.15 K)

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Received: 6 April 2009 / Accepted: 8 April 2009 / Published online: 19 June 2009

Abstract Densities have been measured for the binary mixtures of methanol with ethanol, isomers of propanol and butanol over the entire composition range at 288.15, 293.15, 298.15, 303.15, 308.15, 313.15 K. The density data have been used to calculate the molar volumes, thermal expansion coefficients and their excess values. The excess parameters have been fitted to the Redlich–Kister polynomial equation. The values of the molar volumes, excess molar volumes, thermal expansion coefficients and excess thermal expansion coefficients have been analyzed as a function of the mole fraction and the carbon chain length.

Keywords Alkanols densities · Binary mixtures · Excess properties · Thermal expansion coefficient

Introduction

The study of thermodynamic and transport properties of pure liquids and liquid mixtures are the subject of scientific research in many laboratories for many years. The thermodynamic excess functions such as: molar volume, viscosity, molar enthalpy, acoustic impedance, molar Gibbs energy, refractive index are a source of information about interactions between molecules of the system components. Many workers due to the specific interactions, hydrogen bond effects, hydrophobic effects, etc, have extensively studied thermodynamic properties of binary or ternary mixtures containing alkanols. Most of these papers concern the mixtures of alkanols with water, for example [1–3] or non-polar components [4–7]. A survey of the literature proves that the examined here mixtures composed of two different alkanols [8], especially at the temperatures other than 298.15 K have been much less investigated [2, 9]. The values of thermodynamic excess functions of these systems are smaller than those of alcohol aqueous solutions or alcohol—non-polar liquids systems [8].

In this paper, we present experimental data of densities for binary mixtures of methanol (MeOH) with ethanol (EtOH), 1-propanol (*n*-PrOH), 2-propanol (*i*-PrOH), 1-butanol (*n*-BuOH), 2-methyl-1-propanol (*i*-BuOH), 2-butanol (*s*-BuOH) and 2-methyl-2-propanol (*t*-BuOH) over the whole composition range and at six different temperatures in the interval of 5 K from 288.15 to 313.15 K. The results were used to calculate excess molar volumes V^E and excess thermal expansion coefficient α^E. The changes of V^E values in the binary alkanol mixtures have been examined in many papers [8, 10–24]. Therefore, the values of V^E were compared with those reported earlier. In some papers, the detailed experimental results (density or excess molar volumes) for alcohol binary mixtures are not given directly in the paper, but are given only in figures instead [25] or deposited with the Depository for Unpublished Data, for example [26].

In the literature, we can find the values of expansivities for the pure alkanols at 298.15 K [1, 8, 10, 27–30]. To our knowledge, there are no data of α^E for binary alcohol mixtures in the literature, because it is quite difficult to determine α^E for these mixtures with the necessary accuracy [8]. In that paper, the estimated values of excess isothermal compressions and excess isochoric heat capacities are included errors attributed to the assumption of a zero excess thermal expansion coefficient (α^E is generally not zero in binary mixtures).

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Experimental

Materials

Analytical grade reagents purchased from Merck, Fluka and Aldrich were used. All liquids were stored in dark bottles over molecular sieves (Sigma, 0.3 to 0.4 nm) to reduce water content. Before use, they were double distilled and degassed in an ultrasound bath. The purities of the alcohols were checked by comparison the densities, *d*, and refractive indices, n_D, at 298.15 K with their corresponding literature values (Table 1). The comparison shows a very reasonable agreement.

Measurements

The experimental procedure for densimetric measurements was similar to those described previously [31], only the details of the procedure were modified. Measurements of density were carried out using a bicapillary pycnometer with the volume of about 50 cm^3. A pycnometer was calibrated

Table 1 Experimental and literature densities, d/g cm^{-3}, and refractive indices, n_D, for pure alcohols at 298.15 K

Alcohol	d/g cm^{-3}		n_D	
	This work	Literature	This work	Literature
MeOH	0.78667	0.786573 [8]	1.3266	1.32652 [29, 34]
		0.78665 [13]		1.32645 [13, 35]
		0.78664 [34]		1.3268 [36]
EtOH	0.78510	0.785095 [8]	1.3594	1.35931 [18]
		0.78493 [29]		1.35941 [29, 34]
n-PrOH	0.79960	0.79957 [8, 11]	1.3833	1.38370 [29, 34]
		0.79960 [29]		1.3831 [36]
i-PrOH	0.78101	0.78088 [11]	1.3751	1.37444 [20]
		0.78089 [20]		1.3752 [29, 34]
		0.78126 [29]		
n-BuOH	0.80564	0.805737 [8]	1.3974	1.39741 [29]
		0.80589 [13]		1.39730 [34]
		0.80575 [29]		1.3975 [37]
i-BuOH	0.79774	0.79790 [15]	1.3938	1.39389 [29]
		0.797874 [16]		1.3938 [38]
		0.7978 [29]		
s-BuOH	0.80214	0.802487 [16]	1.3953	1.39488 [19]
		0.80237 [19]		1.39530 [29]
		0.80241 [29]		1.3949 [38]
t-BuOH	0.78077*	0.779479 [16][a]	1.3848*	1.3852 [29]
		0.7812 [29]		1.3850 [38]

*Values extrapolated from the dependence $y = f(x_2)$ for $x_2 = 1$, where y are experimental densities or refractive indices data

[a] Value at 299.15 K

Table 2 Densities values, d /g cm^{-3}, for binary alkanols mixtures at several temperatures

x_2	d/g cm^{-3}					
	T/K					
	288.15	293.15	298.15	303.15	308.15	313.15
MeOH + EtOH						
0.0000	0.79600	0.79133	0.78667	0.78202	0.77738	0.77275
0.0517	0.79585	0.79118	0.78652	0.78191	0.77731	0.77264
0.1023	0.79566	0.79100	0.78635	0.78176	0.77719	0.77256
0.1496	0.79553	0.79088	0.78627	0.78169	0.77713	0.77250
0.2011	0.79535	0.79071	0.78613	0.78157	0.77704	0.77245
0.2490	0.79523	0.79063	0.78605	0.78151	0.77700	0.77241
0.2997	0.79506	0.79049	0.78593	0.78142	0.77692	0.77237
0.3523	0.79496	0.79039	0.78588	0.78137	0.77689	0.77235
0.4021	0.79480	0.79026	0.78577	0.78129	0.77683	0.77233
0.4489	0.79471	0.79021	0.78572	0.78125	0.77681	0.77232
0.5031	0.79456	0.79008	0.78562	0.78117	0.77676	0.77231
0.5487	0.79448	0.79001	0.78557	0.78116	0.77675	0.77230
0.5995	0.79434	0.78990	0.78547	0.78109	0.77671	0.77230
0.6525	0.79425	0.78983	0.78545	0.78106	0.77671	0.77231
0.7017	0.79412	0.78973	0.78536	0.78100	0.77668	0.77231
0.7485	0.79407	0.78968	0.78532	0.78099	0.77668	0.77232
0.8022	0.79394	0.78957	0.78524	0.78093	0.77666	0.77233
0.8497	0.79387	0.78954	0.78522	0.78093	0.77667	0.77235
0.9015	0.79376	0.78944	0.78515	0.78089	0.77665	0.77238
0.9526	0.79370	0.78941	0.78514	0.78090	0.77668	0.77241
1.0000	0.79357	0.78934	0.78510	0.78087	0.77665	0.77244
MeOH + *n*-PrOH						
0.0000	0.79600	0.79133	0.78667	0.78202	0.77738	0.77275
0.0498	0.79673	0.79211	0.78749	0.78292	0.77837	0.77371
0.1003	0.79750	0.79290	0.78837	0.78382	0.77930	0.77470
0.1497	0.79820	0.79365	0.78917	0.78467	0.78024	0.77566
0.1999	0.79893	0.79443	0.79000	0.78556	0.78113	0.77663
0.2501	0.79960	0.79516	0.79077	0.78638	0.78205	0.77757
0.3008	0.80029	0.79591	0.79156	0.78723	0.78290	0.77850
0.3497	0.80090	0.79657	0.79226	0.78798	0.78373	0.77936
0.4004	0.80155	0.79727	0.79299	0.78876	0.78452	0.78021
0.4499	0.80212	0.79788	0.79364	0.78945	0.78529	0.78100
0.5001	0.80272	0.79852	0.79431	0.79016	0.78600	0.78176
0.5503	0.80324	0.79909	0.79491	0.79079	0.78670	0.78248
0.6001	0.80379	0.79966	0.79552	0.79143	0.78733	0.78315
0.6490	0.80427	0.80016	0.79605	0.79198	0.78795	0.78377
0.7004	0.80480	0.80071	0.79663	0.79258	0.78853	0.78439
0.7496	0.80525	0.80117	0.79713	0.79309	0.78908	0.78495
0.7998	0.80574	0.80167	0.79766	0.79363	0.78963	0.78551
0.8503	0.80618	0.80213	0.79814	0.79413	0.79017	0.78606
0.8997	0.80664	0.80261	0.79864	0.79465	0.79068	0.78660
0.9501	0.80708	0.80308	0.79910	0.79514	0.79122	0.78715
1.0000	0.80750	0.80355	0.79960	0.79564	0.79169	0.78773

Table 2 continued

x_2	d/g cm^{-3}					
	T/K					
	288.15	293.15	298.15	303.15	308.15	313.15
MeOH + i-PrOH						
0.0000	0.79600	0.79133	0.78667	0.78202	0.77738	0.77275
0.0501	0.79540	0.79073	0.78608	0.78146	0.77687	0.77221
0.1005	0.79483	0.79018	0.78555	0.78095	0.77638	0.77174
0.1499	0.79431	0.78968	0.78507	0.78049	0.77594	0.77132
0.1990	0.79382	0.78921	0.78463	0.78007	0.77554	0.77094
0.2498	0.79336	0.78877	0.78421	0.77967	0.77516	0.77058
0.3003	0.79292	0.78836	0.78382	0.77930	0.77481	0.77025
0.3490	0.79254	0.78799	0.78347	0.77898	0.77451	0.76997
0.3996	0.79217	0.78764	0.78314	0.77867	0.77422	0.76970
0.4501	0.79182	0.78732	0.78284	0.77839	0.77396	0.76947
0.4997	0.79151	0.78703	0.78257	0.77814	0.77373	0.76926
0.5502	0.79122	0.78676	0.78232	0.77791	0.77353	0.76908
0.6004	0.79095	0.78652	0.78210	0.77771	0.77335	0.76892
0.6503	0.79071	0.78629	0.78190	0.77753	0.77319	0.76878
0.6998	0.79049	0.78610	0.78172	0.77737	0.77305	0.76866
0.7502	0.79029	0.78591	0.78156	0.77723	0.77293	0.76856
0.7999	0.79010	0.78575	0.78141	0.77711	0.77282	0.76848
0.8497	0.78993	0.78560	0.78129	0.77700	0.77274	0.76841
0.9010	0.78977	0.78546	0.78117	0.77690	0.77266	0.76836
0.9502	0.78963	0.78534	0.78107	0.77682	0.77260	0.76831
1.0000	0.78948	0.78524	0.78101	0.77676	0.77253	0.76828
MeOH + n-BuOH						
0.0000	0.79600	0.79133	0.78667	0.78202	0.77738	0.77275
0.0504	0.79726	0.79268	0.78813	0.78359	0.77908	0.77450
0.0999	0.79847	0.79397	0.78948	0.78504	0.78062	0.77615
0.1503	0.79959	0.79520	0.79084	0.78649	0.78214	0.77774
0.1990	0.80070	0.79638	0.79203	0.78775	0.78349	0.77918
0.2491	0.80176	0.79748	0.79327	0.78904	0.78486	0.78058
0.2993	0.80282	0.79860	0.79440	0.79023	0.78608	0.78189
0.3502	0.80379	0.79964	0.79553	0.79140	0.78732	0.78315
0.3999	0.80476	0.80064	0.79652	0.79245	0.78839	0.78429
0.4506	0.80567	0.80159	0.79756	0.79351	0.78948	0.78540
0.4969	0.80650	0.80246	0.79838	0.79437	0.79038	0.78634
0.5503	0.80738	0.80334	0.79937	0.79538	0.79140	0.78737
0.5993	0.80820	0.80418	0.80016	0.79619	0.79225	0.78825
0.6505	0.80895	0.80496	0.80102	0.79706	0.79313	0.78913
0.6993	0.80969	0.80572	0.80172	0.79780	0.79386	0.78991
0.7498	0.81038	0.80641	0.80249	0.79857	0.79465	0.79068
0.7975	0.81105	0.80709	0.80313	0.79920	0.79531	0.79137
0.8513	0.81170	0.80777	0.80387	0.79995	0.79607	0.79212
0.8991	0.81231	0.80839	0.80443	0.80055	0.79667	0.79275
0.9477	0.81286	0.80892	0.80503	0.80116	0.79728	0.79337
1.0000	0.81344	0.80953	0.80564	0.80177	0.79792	0.79402
MeOH + i-BuOH						
0.0000	0.79600	0.79133	0.78667	0.78202	0.77738	0.77275
0.0503	0.79658	0.79197	0.78740	0.78285	0.77828	0.77370
0.1000	0.79716	0.79262	0.78811	0.78363	0.77912	0.77460
0.1502	0.79776	0.79327	0.78881	0.78438	0.77993	0.77546
0.1999	0.79836	0.79392	0.78949	0.78511	0.78070	0.77627
0.2499	0.79895	0.79455	0.79016	0.78582	0.78145	0.77706
0.2998	0.79954	0.79517	0.79082	0.78651	0.78218	0.77783
0.3502	0.80010	0.79577	0.79145	0.78719	0.78290	0.77858
0.3995	0.80063	0.79634	0.79206	0.78784	0.78359	0.77931
0.4502	0.80114	0.79689	0.79266	0.78849	0.78428	0.78005
0.4996	0.80161	0.79741	0.79322	0.78911	0.78495	0.78077
0.5502	0.80207	0.79792	0.79377	0.78972	0.78562	0.78149
0.5992	0.80247	0.79838	0.79428	0.79029	0.78624	0.78217
0.6501	0.80287	0.79884	0.79479	0.79087	0.78687	0.78285
0.6991	0.80324	0.79926	0.79526	0.79139	0.78745	0.78349
0.7490	0.80359	0.79967	0.79571	0.79190	0.78801	0.78409
0.7997	0.80396	0.80007	0.79616	0.79238	0.78853	0.78465
0.8501	0.80432	0.80047	0.79658	0.79283	0.78900	0.78515
0.8998	0.80471	0.80085	0.79698	0.79322	0.78940	0.78555
0.9497	0.80512	0.80125	0.79737	0.79356	0.78973	0.78586
1.0000	0.80559	0.80166	0.79774	0.79385	0.78997	0.78605
MeOH + s-BuOH						
0.0000	0.79600	0.79133	0.78667	0.78202	0.77738	0.77275
0.0500	0.79714	0.79253	0.78793	0.78335	0.77880	0.77416
0.1001	0.79825	0.79365	0.78910	0.78458	0.78009	0.77554
0.1503	0.79921	0.79473	0.79026	0.78580	0.78135	0.77684
0.1999	0.80016	0.79571	0.79127	0.78686	0.78248	0.77806
0.2503	0.80108	0.79668	0.79230	0.78795	0.78363	0.77922
0.2990	0.80186	0.79751	0.79319	0.78889	0.78460	0.78027
0.3502	0.80271	0.79839	0.79411	0.78986	0.78562	0.78131
0.3997	0.80344	0.79915	0.79491	0.79068	0.78650	0.78225
0.4501	0.80413	0.79993	0.79573	0.79155	0.78738	0.78315
0.4991	0.80479	0.80058	0.79641	0.79226	0.78815	0.78397
0.5489	0.80545	0.80128	0.79713	0.79301	0.78890	0.78474
0.6001	0.80607	0.80191	0.79779	0.79369	0.78961	0.78548
0.6492	0.80665	0.80254	0.79843	0.79435	0.79027	0.78614
0.7004	0.80725	0.80310	0.79900	0.79492	0.79088	0.78677
0.7500	0.80777	0.80378	0.79960	0.79552	0.79147	0.78735
0.8004	0.80835	0.80422	0.80011	0.79604	0.79199	0.78788
0.8487	0.80886	0.80476	0.80064	0.79657	0.79249	0.78836
0.9002	0.80942	0.80526	0.80115	0.79703	0.79295	0.78883
0.9502	0.80999	0.80579	0.80164	0.79751	0.79343	0.78925
1.0000	0.81053	0.80632	0.80214	0.79797	0.79383	0.78964
MeOH + t-BuOH						
0.0000	0.79600	0.79133	0.78667	0.78202	0.77738	0.77275

Table 2 continued

x_2	d/g cm^{-3}					
	T/K					
	288.15	293.15	298.15	303.15	308.15	313.15
0.0503	0.79518	0.79059	0.78601	0.78144	0.77690	0.77232
0.0989	0.79449	0.78999	0.78548	0.78095	0.77652	0.77199
0.1505	0.79381	0.78939	0.78493	0.78048	0.77613	0.77169
0.2010	0.79326	0.78891	0.78451	0.78013	0.77585	0.77145
0.2490	0.79279	0.78849	0.78416	0.77982	0.77559	0.77126
0.3012	0.79240	0.78816	0.78387	0.77959	0.77540	0.77110
0.3488	0.79209	0.78789	0.78363	0.77940	0.77524	0.77100
0.3999	0.79188	0.78771	0.78347	0.77927	0.77514	0.77090
0.4505	0.79171	0.78756	0.78334	0.77914	0.77503	0.77083
0.4998	0.79165	0.78750	0.78327	0.77908	0.77497	0.77075
0.5503	0.79160	0.78744	0.78320	0.77899	0.77487	0.77065
0.5977	0.79164	0.78745	0.78319	0.77893	0.77479	0.77052
0.6478	0.79168	0.78744	0.78312	0.77880	0.77463	0.77032
0.7014	0.79178	0.78747	0.78306	0.77866	0.77442	0.77001
0.7508	0.79184	0.78743	0.78292	0.77842	0.77411	0.76961
0.7980	0.79193	0.78741	0.78277	0.77815	0.77373	0.76909
0.8487	0.79195	0.78727	0.78247	0.77773	0.77314	0.76836
0.9011	0.79195	0.78709	0.78206	0.77713	0.77238	0.76738
0.9511	0.79186*	0.78675	0.78148	0.77636	0.77137	0.76616
1.0000	0.79167*	0.78631*	0.78077*	0.77547	0.77020	0.76473

*values extrapolated from the dependence $d = f(x_2)$ for $x_2 = 1$, where d are experimental densities

with extra pure water, previously degassed ultrasonically. All the solutions were prepared by mass using an analytical balance (Sartorius RC 210D) with a precision of ± 1×10^{-5} g. A pycnometer was thermostatted with the accuracy better than 0.01 K using a precise thermostat (Julabo, MHF 32, Germany). The temperature was controlled by a calibrated digital thermometer (Anton Paar, DT 100-20) with an accuracy of ±0.01 K.

The refractive indices were measured using digital Abbe refractometer AR 2008.

The densities are accurate to 2×10^{-5} g cm^{-3}, the refractive index and the mole fraction are accurate to 1×10^{-4}, and the molar volumes to 5×10^{-3} cm^3 mol^{-1}.

Results and discussion

The experimental values of density for the seven binary mixtures at 288.15, 293.15, 298.15, 303.15, 308.15, 313.15 K are reported in Table 2.

The values of excess molar volumes V^E were derived from density using the following formula [32]:

$$V^{E} = (x_1M_1 + x_2M_2)/d - x_1M_1/d_1 - x_2M_2/d_2 \quad (1)$$

where x_i, M_i, d_i are the mole fraction, the molar mass and the density of component i and d is the density of the mixture, respectively.

The values of excess molar volumes V^E were fitted to the Redlich–Kister equation:

$$V^{E} = x_1 x_2 \sum_{i=0}^{n} a_i (x_2 - x_1)^i \quad (2)$$

to obtain the parameters a_i; n is the degree of the polynomic expansion. The linear last squares fitting procedure was used to fit the polynomials to the data. The adjustable parameters a_i, their standard errors and the standard deviations σ (V^E) are listed in Table 3.

The standard errors of all fits indicate that the above equation fits the experimental data very well.

The data from Table 3 were used to determine the smoothed values of molar volumes. The molar volumes V for the binary mixtures at 298.15 K are summarized in Table 4.

Among isomeric alcohols the molar volume values change as follows:

$$V_{i\text{-PrOH}} > V_{n\text{-PrOH}}$$
$$V_{t\text{-BuOH}} > V_{i\text{-BuOH}} > V_{s\text{-BuOH}} > V_{n\text{-BuOH}}$$

As can be seen, the molar volume of alcohol increases with a degree of branching of the alcohol molecule. One

Table 3 Coefficients of the Redlich–Kister Eq. 2 and their standard errors for excess molar volume, V^E, at 298.15 K

Mixture	a_i			$\sigma(V^E)$
	a_o	a_1	a_2	
MeOH + EtOH	0.0297 ± 0.0028	−0.0066 ± 0.0035	0.1406 ± 0.0071	0.001
MeOH + *n*-PrOH	0.2179 ± 0.0034	−0.0551 ± 0.0041	0.1058 ± 0.0085	0.001
MeOH + *i*-PrOH	0.1162 ± 0.0021	0.0487 ± 0.0026	0.0141 ± 0.0053	0.001
MeOH + *n*-BuOH	0.4510 ± 0.0035	−0.1736 ± 0.0043	0.0670 ± 0.0087	0.001
MeOH + *i*-BuOH	0.3868 ± 0.0010	−0.1403 ± 0.0012	0.0306 ± 0.0025	0.001
MeOH + *s*-BuOH	0.3199 ± 0.0032	−0.0661 ± 0.0039	0.0978 ± 0.0080	0.001
MeOH + *t*-BuOH	−0.2541 ± 0.0062	−0.8006 ± 0.0076	−0.6079 ± 0.0155	0.002

Table 4 The molar volumes, V/cm^3 mol^{-1}, for the binary mixtures at 298.15 K

x_2	MeOH + EtOH	MeOH + *n*-PrOH	MeOH + *i*-PrOH	MeOH + *n*-BuOH	MeOH + *i*-BuOH	MeOH + *s*-BuOH	MeOH + *t*-BuOH
0.0000	40.729	40.729	40.729	40.729	40.729	40.729	40.729
0.0500	41.628	42.467	42.544	43.324	43.363	43.334	43.438
0.1000	42.528	44.202	44.359	45.913	45.994	45.935	46.149
0.1500	43.427	45.933	46.173	48.497	48.620	48.533	48.860
0.2000	44.325	47.662	47.988	51.076	51.243	51.127	51.570
0.2500	45.223	49.388	49.802	53.651	53.862	53.718	54.278
0.3000	46.121	51.113	51.616	56.222	56.478	56.307	56.983
0.3500	47.019	52.836	53.430	58.790	59.091	58.894	59.684
0.4000	47.917	54.558	55.244	61.355	61.702	61.479	62.382
0.4500	48.814	56.279	57.057	63.917	64.311	64.063	65.076
0.5000	49.712	58.000	58.869	66.478	66.917	66.646	67.767
0.5500	50.609	59.720	60.681	69.036	69.522	69.227	70.456
0.6000	51.507	61.440	62.493	71.593	72.125	71.808	73.145
0.6500	52.404	63.159	64.304	74.148	74.727	74.387	75.836
0.7000	53.301	64.877	66.114	76.702	77.328	76.965	78.530
0.7500	54.198	66.595	67.923	79.255	79.927	79.543	81.230
0.8000	55.095	68.311	69.731	81.806	82.526	82.118	83.939
0.8500	55.992	70.027	71.538	84.357	85.124	84.693	86.660
0.9000	56.888	71.741	73.344	86.906	87.721	87.265	89.396
0.9500	57.785	73.453	75.149	89.454	90.317	89.835	92.152
1.0000	58.680	75.163	76.952	92.001	92.912	92.403	94.932*

*Extrapolated volume

can also notice that the biggest molar volume is found for tertiary alcohols, the smallest in primary ones.

As shown in Fig. 1 in the case of all mixtures of methanol with other alcohols (except for mixtures with *tert*-butanol) V^E value is positive. In the mixture of methanol + ethanol, almost ideal behaviour is observed [8, 18].

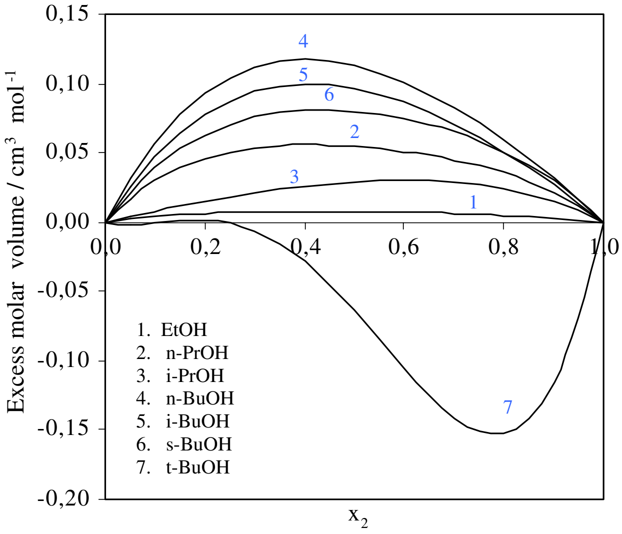

Fig. 1 Excess molar volume, V^E, as a function of the mole fraction for binary alkanols mixtures at 298.15 K

In the case of mixtures of methanol with *tert*-butanol the V^E value is negative. Definitely negative excess V^E values in mixtures with *tert*-butanol prove a tendency of these mixtures for a more close-packed structure. In the system methanol + *tert*-butanol biggest compression occurs with the contents of 0.8 mole fraction of *tert*-butanol. It is possible to assume that molecules of methanol place themselves in free spaces between molecules *tert*-butanol. It may be connected with forming of the intermolecular hydrogen bonds. The values of V^E can be ordered depending on the length of a carbon chain of the same type (primary, secondary or tertiary):

$$V^E_{n-\text{BuOH}} > V^E_{n-\text{PrOH}} > V^E_{\text{EtOH}} \text{ and } V^E_{s-\text{BuOH}} > V^E_{i-\text{PrOH}}$$

And according to the type of alcohol:

$$V^E_{n-\text{PrOH}} > V^E_{i-\text{PrOH}} \text{ and } V^E_{n-\text{BuOH}} > V^E_{s-\text{BuOH}} > V^E_{t-\text{BuOH}}$$

The V^E values are relatively small in binary alcohols mixtures, sometimes on the level of accuracy resulting from the experimental method adopted. That is essential for the assessment of the accuracy of the method used, finding the molar volume in a wide range of temperatures. Such examinations have not been carried out for mixtures of this type so far. Only in a few cases these data are available [2, 9].

It is interesting to compare the excess function behaviour with that of the same systems available in the literature

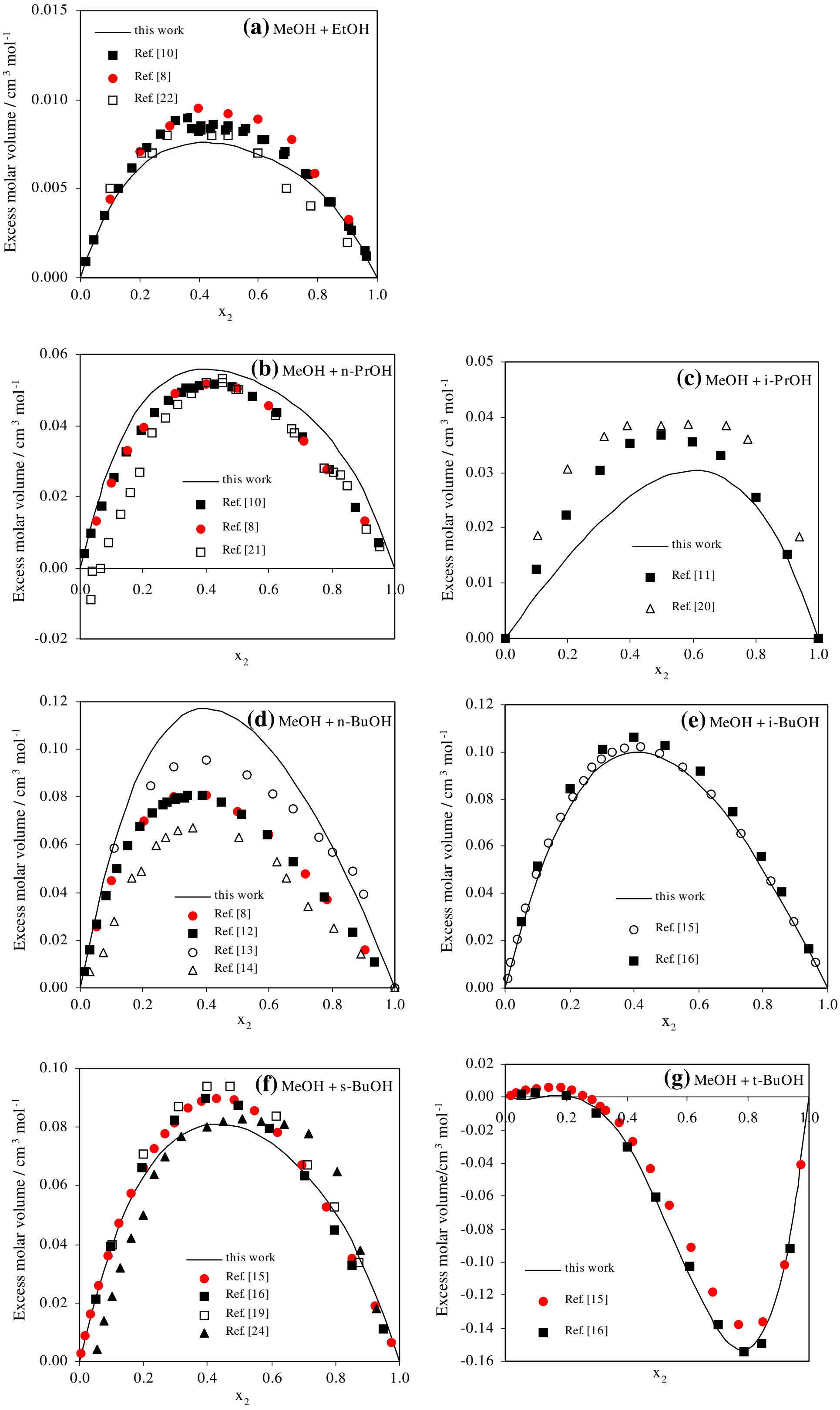

Fig. 2 **a**–**g** Comparison of excess molar volume, V^E, for binary alkanols mixtures at 298.15 K with those reported in literature. The full line shows our results, points-literature data

(Fig. 2a–g). The values of excess molar volumes for methanol + ethanol system presented in paper [18] are negative, maximum of the order of $-0.013\ \mathrm{cm^3\ mol^{-1}}$, and are not presented here. Our values are in good agreement with the values obtained by the more accurate method of volume dilatometry, particularly considering the fact

Table 5 Values of thermal expansion coefficient$\alpha = (\partial \ln V/\partial T)_{298.15\ \mathrm{K}}$

x_2	MeOH + EtOH $10^3 \cdot \alpha/\mathrm{K}^{-1}$	MeOH + *n*-PrOH	MeOH + *i*-PrOH	MeOH + *n*-BuOH	MeOH + *i*-BuOH	MeOH + *s*-BuOH	MeOH + *t*-BuOH
0.0000	1.183	1.183	1.183	1.183	1.183	1.183	1.183
	1.196[a]	1.201[b]	1.185[c]				
0.0500	1.181	1.169	1.179	1.156	1.162	1.166	1.162
0.1000	1.177	1.154	1.175	1.131	1.145	1.150	1.143
0.1500	1.172	1.140	1.171	1.108	1.131	1.134	1.125
0.2000	1.167	1.126	1.166	1.088	1.119	1.119	1.110
0.2500	1.161	1.112	1.161	1.070	1.108	1.104	1.097
0.3000	1.155	1.099	1.156	1.054	1.098	1.091	1.086
0.3500	1.150	1.086	1.151	1.040	1.088	1.078	1.077
0.4000	1.144	1.074	1.146	1.028	1.076	1.066	1.071
0.4500	1.138	1.064	1.141	1.018	1.064	1.056	1.068
0.5000	1.132	1.054	1.136	1.009	1.051	1.047	1.069
0.5500	1.127	1.045	1.131	1.001	1.036	1.039	1.073
0.6000	1.122	1.036	1.126	0.995	1.022	1.033	1.081
0.6500	1.117	1.029	1.122	0.990	1.007	1.028	1.095
0.7000	1.112	1.022	1.117	0.985	0.993	1.025	1.113
0.7500	1.108	1.016	1.112	0.982	0.980	1.023	1.138
0.8000	1.103	1.011	1.107	0.978	0.969	1.023	1.169
0.8500	1.098	1.005	1.102	0.975	0.963	1.025	1.208
0.9000	1.092	1.000	1.097	0.972	0.961	1.029	1.254
0.9500	1.085	0.995	1.091	0.968	0.966	1.034	1.310
1.0000	1.078	0.989	1.085	0.964	0.980	1.042	1.376
	1.096[a]	1.004[a]	1.064[a]	0.948[a]	0.95[a]	1.024[a]	1.325[a]
	1.092[b]	1.003[b]		0.937[c]			
	1.083[c]	0.981[c]					

Values for pure alcohols: [a][29], [b][1], [c][10], [d][39]

that V^E values are very small. Therefore, one can assume that the accuracy of the volumetric data studied here at different temperatures is also entirely satisfactory.

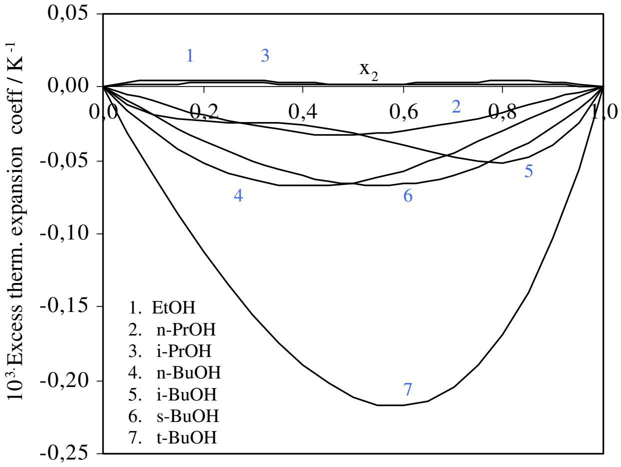

Fig. 3 Excess thermal expansion coefficient, α^E, as a function of the mole fraction for binary alkanols mixtures at 298.15 K

Thermal expansion coefficients α for each mixture were calculated from the experimental densities at different temperatures as:

$$\alpha = \frac{\left(\frac{\partial V}{\partial T}\right)_p}{V} = \left(\frac{\partial \ln V}{\partial T}\right)_p = -\frac{\partial \ln d}{\partial T} \tag{3}$$

where T is the temperature, V is the volume, d is the density, and derivatives are taken at constant pressure p.

Next, the excess thermal expansion coefficients α^E were obtained. The Redlich–Kister procedure was adjusted to the calculated values, in a similar way as previously, and the smoothed values of coefficients α were calculated. The values of thermal expansion coefficients $\alpha = (\partial \ln V/\partial T)_{298.15\ \mathrm{K}}$are summarized in Table 5.

As seen from the data collected in Table 5, values of thermal expansion coefficients α for pure alkanols are in good agreement with literature data. All the values are positive, because the intermolecular distance increases with increasing temperature. It is possible for pure alcohol to place the α value in the order:

$$\alpha_{t-\mathrm{BuOH}} > \alpha_{\mathrm{MeOH}} > \alpha_{i-\mathrm{PrOH}} > \alpha_{\mathrm{EtOH}} > \alpha_{s-\mathrm{BuOH}} > \alpha_{n-\mathrm{PrOH}} > \alpha_{i-\mathrm{BuOH}} > \alpha_{n-\mathrm{BuOH}}$$

For different types of alcohols (primary, secondary and tertiary):

$$\alpha_{t-\mathrm{BuOH}} > \alpha_{s-\mathrm{BuOH}} > \alpha_{i-\mathrm{BuOH}} \cong \alpha_{n-\mathrm{BuOH}} \text{ and } \alpha_{i-\mathrm{PrOH}} > \alpha_{n-\mathrm{PrOH}}$$

However, a comparison of value α for alcohol of the same type but different chain length, gives the following dependencies:

$$\alpha_{\mathrm{MeOH}} > \alpha_{\mathrm{EtOH}} > \alpha_{n-\mathrm{PrOH}} > \alpha_{n-\mathrm{BuOH}} \text{ and } \alpha_{i-\mathrm{PrOH}} > \alpha_{s-\mathrm{BuOH}}$$

The same order is given in papers [1, 10, 27, 28, 30]. As can be seen, the thermal expansion coefficient of alkanols decreases with increasing chain length. It is well known that in the case of *n*-alkanols the hydrogen bond density is larger for smaller molecules [33]. This would explain the order mentioned above. The addition of alcohol to methanol decreases the values of α. However, in the mixtures rich of co-solvent we can see the other course of the dependence $\alpha = f\ (x_2)$. The α values decrease for MeOH + EtOH, MeOH + *i*-PrOH, MeOH + *n*-PrOH mixtures, they stabilize for MeOH + *n*-BuOH, MeOH + *i*-BuOH, MeOH + *s*-BuOH, and they increase for MeOH + *t*-BuOH.

Figure 3 represents the plot of the excess thermal expansion coefficient α versus mole fraction of alkanol at $T = 298.15$ K.

The coefficients of the Redlich–Kister equation, their standard errors and the standard deviations for the excess thermal expansion coefficients α^{E} are listed in Table 6.

For all systems studied here, the excess values of thermal expansion coefficients α^{E} are negative or close to zero. The most negative excess values are present in mixtures of methanol with *tert*-butanol. In other cases the values are definitely less negative. The excess thermal expansion coefficients are the following:

$$\alpha^{\mathrm{E}}_{\mathrm{EtOH}} > \alpha^{\mathrm{E}}_{n-\mathrm{PrOH}} > \alpha^{\mathrm{E}}_{n-\mathrm{BuOH}} \text{ and } \alpha^{\mathrm{E}}_{i-\mathrm{PrOH}} > \alpha^{E}_{s-\mathrm{BuOH}}$$

It is possible to assume that the larger is the difference of chain length between methanol and the other alcohols, the more negative is the excess value of this coefficient.

Considering the type of the alcohol added to methanol (primary, secondary or tertiary), values of α^{E} change in the order:

$$\alpha^{\mathrm{E}}_{n-\mathrm{BuOH}} \cong \alpha^{\mathrm{E}}_{s-\mathrm{BuOH}} > \alpha^{\mathrm{E}}_{t-\mathrm{BuOH}}$$

As mentioned above, in the literature there are no data of α^{E} for binary alcohols mixtures. However, density data measured at some temperatures were reported [2, 9]. Therefore, we calculated values of α^{E} for methanol + ethanol and methanol + *n*-propanol systems at 298.15 K. Data α^{E} from paper [9] are in good agreement with our data (especially for methanol + ethanol). The values of α^{E} for methanol + ethanol calculated on the basis of data from paper [2] are a little lower than our.

Conclusions

The densities of binary alcohol mixtures (methanol with ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 2-butanol and 2-methyl-2-propanol) were measured over the whole composition range at T = 288.15, 293.15, 298.15, 303.15, 308.15, 313.15 K and atmospheric pressure. The excess molar volumes V^{E} and excess thermal expansion coefficient α^{E} were determined from experimental results of density and fitted to the Redlich–Kister polynomial equation. Excess molar volumes at 298.15 K are positive for the systems studied here (except of *tert*-butanol) and they are in agreement with those reported earlier. The excess thermal expansion coefficients α^{E} are negative or close to zero. The most negative excess values of V^{E} and α^{E} appear in mixtures of methanol with *tert*-butanol. It has been demonstrated that the excess thermal expansion coefficients depend on carbon chain length and branching of alkanols added to methanol.

Table 6 Coefficients of the Redlich–Kister equation and their standard errors for the excess thermal expansion coefficients, α^{E}, at 298.15 K

Mixture	$10^4 \cdot a_i$		
	$10^4 \cdot a_o$	$10^4 \cdot a_1$	$10^4 \cdot a_2$
MeOH + EtOH	0.0724 ± 0.0125	−0.0878 ± 0.0152	0.5685 ± 0.0312
MeOH + *n*-PrOH	−1.2969 ± 0.0081	0.0665 ± 0.0099	0.5195 ± 0.0202
MeOH + *i*-PrOH	0.0865 ± 0.0064	0.0086 ± 0.0078	0.1858 ± 0.0160
MeOH + *n*-BuOH	−2.5929 ± 0.0076	1.1098 ± 0.0093	0.2074 ± 0.0190
MeOH + *i*-BuOH	−1.2340 ± 0.0110	−1.4890 ± 0.0134	−3.0257 ± 0.0274
MeOH + *s*-BuOH	−2.6154 ± 0.0085	−0.5797 ± 0.0103	0.0324 ± 0.0211
MeOH + *t*-BuOH	−8.4286 ± 0.0076	−2.9879 ± 0.0092	−0.8807 ± 0.0188

Acknowledgements Research sponsored by Polish State Committee for Scientific Research (Grant No 505/241).

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