Densities, viscosities, excess molar volumes, and refractive indices of acetonitrile and 2-alkanols binary mixtures at different temperatures: Experimental results and application of the Prigogine–Flory–Patterson theory

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ABSTRACT

Densities, viscosities, and refractive indices of mixing of acetonitrile with 2-propanol, 2-butanol, 2-pentanol, 2-hexanol and 2-heptanol, have been measured as a function of composition at 293.15, 298.15, 303.15 and 308.15 K and ambient pressure. The excess molar volumes, viscosity and refractive index deviations calculated and fitted to Redlich–Kister polynomials. From the experimental data, partial molar volumes, $\bar{V}_{m,i}$ and partial molar volumes at infinite dilution, $\overline{V^o_{m,i}}$ were also calculated. The latter values are interesting from a theoretical point of view since at infinite dilution the only interactions present are solute solvent interactions. For mixtures of acetonitrile with used 2-alkanols, over the entire range of mole fractions, $\Delta\eta$ is negative and both, V^E_m and Δn_D are positive. The effect of temperature and chain-length of the 2-alkanols on the excess molar volumes, viscosity and refractive index deviations of its mixtures with acetonitrile are discussed in terms of molecular interaction between unlike molecules. The experimental results have been used to test the applicability of the Prigogine–Flory–Patterson (PFP) theory.

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1. Introduction

The thermodynamic and transport properties of liquids and liquid mixtures have been used to understand the molecular interactions between the components of the mixture and also for engineering applications concerning heat transfer, mass transfer and fluid flow [1]. Density, viscosity and refractive index data of binary liquid mixtures are very important from theoretical point of view, to understand liquid theory. Acetonitrile, alkanols, and their binary mixtures find applications as solvent in chemistry and modern technology [2].

A survey of literatures shows that there are very few reports on the density, viscosity, and refractive index of acetonitrile + 2-alkanols. This paper is a part of an ongoing research effort to measure and characterize the properties of mixtures containing 2-alkanols [3–5]. We present, here, densities, viscosities, refractive indices, excess molar volumes, viscosity and refractive index deviations of mixing for the binary mixtures of {acetonitrile + 2-alkanols} at the temperatures of 293.15, 298.15, 303.15 and 308.15 K. To the best of our knowledge, no much data are reported for mixtures with acetonitrile and 2-alkanols at the comparable conditions of this study.

2. Experimental

2.1. Materials purities and suppliers

Acetonitrile (mass fraction > 0.99), 2-propanol (mass fraction 0.99), 2-butanol (mass fraction 0.99), 2-pentanol (mass fraction > 99), 2-hexanol (mass fraction > 0.99) and 2-heptanol (mass fraction > 0.99) were purchased from Merck and used without further purifications. The experimental densities, viscosities and refractive indices at 298.15 K of the pure materials are presented in Table 1 along with the corresponding literature values [2,3,6–8].

2.2. Apparatus and procedure

Densities of the pure liquids and their mixtures at various temperatures were measured with an Anton Paar digital densimeter (Model DMA 4500) operated in the static mode, with an accuracy of $\pm 1 \times 10^{-5}$. Viscosities were measured with an Ubbleohde viscometer with an accuracy of $\pm 2 \times 10^{-5}$. The equation for viscosity, according to Poiseuille's law, is

$$\eta = \rho \left(kt - \frac{c}{t} \right) \tag{1}$$

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Table 1
Experimental and literature values of densities ρ, viscosities η, and refractive indices n_D, of acetonitrile, 2-propanol, 2-butanol, 2-pentanol, 2-hexanol and 2-heptanol at 298.15 K.

Compound	ρ (g cm^{-3})		η (mPa s)		n_D	
	Exp.	Lit.	Expt.	Lit.	Expt.	Lit.
Acetonitrile	0.77664	0.7766[7]	0.3369	0.342[2]	1.3411	1.34163[7]
2-Propanol	0.78098	0.78126[7]	2.0439	2.0436[2]	1.3745	1.3752[7]
2-Butanol	0.80256	0.80260[7]	3.1318	3.1150[6]	1.3948	1.3950[7]
2-Pentanol	0.80524	0.80540[7]	3.4785	3.47[8]	1.4045	1.4044[7]
2-Hexanol	0.81014	0. 81025[3]	4.1	4.204[3]		1.4116
2-Heptanol	0.81333	0.8134[7]	5.3305	5.346[3]		1.4188

where k and c are the viscometer constants t and η are the efflux time and dynamic viscosity, respectively. The k and c parameters were obtained by measurements on double distilled water and benzene at 298.15 K. The temperature in the cell was regulated to ±0.01 K.

Refractive indices were measured using a high accuracy Abbe refractometer with an accuracy of ±4 × 10^{-5}. The measurement method relies on an optical detection of the critical angle at the wavelength of the sodium D line (589.6 nm). The mixtures were prepared by weighing known masses of pure liquids in air tight, narrow-mouth ground stoppered bottles taking due precautions to minimize evaporation losses. All the mass measurements were performed on an electronic balance (Mettler AE 163, Switzerland) accurate to 0.01 mg. The possible error in the mole fraction is estimated to be less than ±1 × 10^{-4}.

3. Results and discussion

3.1. Densities and excess molar volumes

The excess molar volumes of the solutions of molar composition x were calculated from the densities of the pure liquids and their mixtures according to the following equation

$$V_m^E = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \qquad (2)$$

where ρ is the density of the mixture, ρ_i is the density of pure component i, x_i is the mole fraction, M_i is the molar mass of component i, and N stands for the number of components in the mixture.

The corresponding V_m^E values of binary mixtures of [x_1 acetonitrile + (1 − x_1) 2-alkanols] measured at different temperatures are plotted against mole fraction of acetonitrile at 298.15 K in Fig. 1.

Each set of results were fitted using a Redlich–Kister polynomial [9] which for binary mixtures is

$$Y^E = x_1(1 - x_1) \sum_{k=0}^{N} A_k (1 - 2x_1)^k \qquad (3)$$

where $Y^E \equiv V_m^E$ or $\Delta \eta$ or Δn_D and x_1 is the mole fraction of acetonitrile, A_k are adjustable parameters obtained by least-squares method, and k is the degree of the polynomials.

In each case, the optimum number of coefficients was ascertained from an examination of the variation of standard deviation σ with

$$\sigma = \left[\frac{\sum (Y_{exp.} - Y_{cal.})^2}{(n - p)} \right]^{1/2} \qquad (4)$$

where $Y_{exp.}$ and $Y_{cal.}$ are the experimental and calculated values of the property Y, respectively, and n and p are the number of experimental points and number of parameters retained in the respective equations.

Table 2 presents the values of the parameters A_k together with the standard deviation σ. The coefficients A_k were used to calculate the solid curves in Fig. 1. Excess molar volumes are positive for mixtures of acetonitrile with 2-alkanols over the whole range of mole fractions. Fig. 1 shows that, V_m^E at equimolar concentrations of acetonitrile, increases from 2-propanol up to 2-heptanol, as the length of the alkanols chain increases.

The same behavior is obtained at other temperatures, except that the values of V_m^E become more Positive with increase in temperature.

The observed V_m^E can be considered as arising from two types of interactions between the components: (i) physical interaction consist mainly dispersion forces and making a positive contribution, and (ii) chemical or specific interaction resulting in a volume decrease. The latter includes charge transfer forces, forming and/or
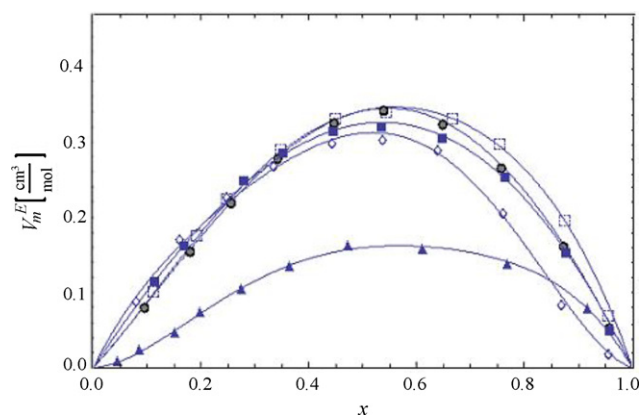

Fig. 1. Excess molar volumes V_m^E vs. mole fraction of acetonitrile for acetonitrile binary mixtures with (▲) 2-propanol, (◇) 2-butanol, (■) 2-pentanol, (●) 2-hexanol, (□) 2-heptanol at 298.15 K. The solid curves were calculated from coefficients of Eq. (3) given in Table 2.
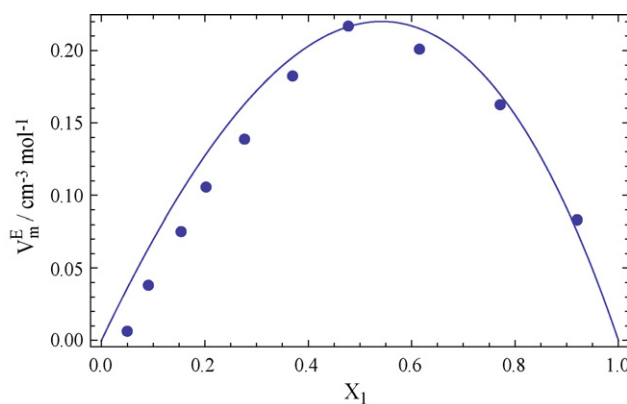

Fig. 2. Plot of excess molar volume V_m^E against mole fraction of acetonitrile for the {x_1 acetonitrile + (1 − x_1) 2-propanol} mixtures. (●) Experimental; (− −) calculated by using PFP theory.

Table 2
Parameters and standard deviations of Eqs. (3) and (4) for acetonitrile + 2 alkanols at different temperatures.

		Temperature	A_0	A_1	A_2	A_3	σ
Acetonitrile + 2-propanol	V_m^E (cm^3 mol^{-1})	293.15	0.6394	−0.1539	0.0088	−0.4421	0.003
		298.15	0.8407	−0.1006	−0.1343	−0.4601	0.006
		303.15	0.9144	−0.0960	−0.0460	−0.3896	0.005
		308.15	1.028	−0.1214	−0.2983	−0.2862	0.001
	$\Delta\eta$ (mPa s)	293.15	−2.9410	−1.9301	−1.4723	−0.6149	0.009
		298.15	−2.4568	−1.4489	−1.4642	−0.9840	0.004
		303.15	−2.048	−1.1176	−1.1363	−0.7532	0.003
		308.15	−1.7352	−0.9349	−0.8138	−0.5752	0.003
	Δn_D	293.15	0.0125	−0.0102	0.0015	0.0014	0.00005
		298.15	0.0208	−0.0051	−0.0048	−0.0009	0.0001
		303.15	0.0169	0.0012	0.0082	−0.0138	0.0002
		308.15	0.0238	0.0022	0.0039	−0.0202	0.0003
Acetonitrile + 2-butanol	V_m^E (cm^3 mol^{-1})	293.15	1.2481	−0.1305	−0.4009	0.7341	0.007
		298.15	1.3547	−0.0223	0.0973	0.1967	0.006
		303.15	1.3926	−0.0316	0.1749	−0.1837	0.003
		308.15	1.4622	0.0016	−0.2378	−0.3579	0.005
	$\Delta\eta$ (mPa s)	293.15	−5.3910	−3.5409	−4.4644	−4.2187	0.009
		298.15	−4.1111	−2.5578	−2.9842	−2.6724	0.001
		303.15	−3.1527	−1.8637	−1.9971	−1.6378	0.006
		308.15	−2.6069	−1.5344	−1.6050	−1.2956	0.0002
	Δn_D	293.15	0.0289	0.0101	0.0068	−0.0030	0.00005
		298.15	0.0305	−0.0023	−0.0009	−0.0077	0.00005
		303.15	0.0358	0.0104	−0.0040	−0.0173	0.00008
		308.15	0.0369	−0.0159	0.0124	−0.0187	0.0001
Acetonitrile + 2-pentanol	V_m^E (cm^3 mol^{-1})	293.15	1.2982	−0.1878	−0.0156	−0.0087	0.004
		298.15	1.340	−0.2918	−0.026	−0.1584	0.003
		303.15	1.4179	−0.2064	−0.0431	0.0163	0.005
		308.15	1.4581	−0.2232	−0.0476	−0.0351	0.002
	$\Delta\eta$ (mPa s)	293.15	−5.6808	−3.6033	−4.088	−3.3281	0.024
		298.15	−4.3811	−2.8846	−2.4687	−1.082	0.047
		303.15	−3.2071	−1.8007	−1.5014	−0.7396	0.006
		308.15	−2.6469	−1.4531	−1.3176	−0.8693	0.005
	Δn_D	293.15	0.0527	−0.0102	−0.0095	0.0192	0.0001
		298.15	0.0568	−0.0063	0.0158−	−0.0079	0.0001
		303.15	0.0609	−0.0073	−0.0105	−0.0069	0.0009
		308.15	0.0669	−0.0396	−0.0301	0.0483	0.0009
Acetonitrile + 2-hexanol	V_m^E (cm^3 mol^{-1})	293.15	1.3656	−0.3098	−0.2335	−0.0135	0.001
		298.15	1.4115	−0.3362	−0.2574	−0.0239	0.002
		303.15	1.4122	−0.2496	0.0207	−0.4043	0.003
		308.15	1.4452	−0.2402	−0.2829	−0.3496	0.004
	$\Delta\eta$ (mPa s)	293.15	−6.4860	−3.6654	−3.5826	−2.7317	0.030
		298.15	−4.8490	−2.6035	−2.1334	−1.3399	0.010
		303.15	−3.8441	−1.9671	−1.6201	−0.9541	0.007
		308.15	−2.9752	−1.4529	0.9902	−0.4597	0.003
	Δn_D	293.15	0.0616	−0.0197	0.0048	−0.0193	0.0004
		298.15	0.0731	−0.0190	−0.0026	−.0014	0.0002
		303.15	0.0831	0.0279−	−0.0002	0.0075	0.0005
		308.15	0.0902	−0.0189	0.0233	−0.0450	0.0002
Acetonitrile + 2-heptanol	V_m^E (cm^3 mol^{-1})	293.15	1.3669	−0.3139	0.0617	−0.3491	0.006
		298.15	1.4065	−0.1915	−0.0562	−0.5971	0.009
		303.15	1.4232	−0.2107	−0.1502	−0.3058	0.005
		308.15	1.5212	−0.0152	−0.3250	−1.1118	0.007
	$\Delta\eta$ (mPa s)	293.15	−8.1686	−4.6000	−3.2429	−2.3763	0.028
		298.15	−6.3674	−3.2978	−2.5122	−2.3887	0.020
		303.15	−4.8318	−2.3522	−1.4507	−1.3395	0.019
		308.15	−3.6669	−1.5195	−0.8862	−1.1093	0.017
	Δn_D	293.15	0.0774	−0.0285	−0.0025	−0.0097	0.0003
		298.15	0.0839	−0.0177	0.0081	−0.0351	0.0003
		303.15	0.0907	−0.0139	0.0046	−0.0523	0.0002
		308.15	0.0907	−0.0139	0.0046	−0.0523	0.0003

breaking of H bonds and other complex forming interactions. It is well-known that both acetonitrile and 2-alkanols are associated in liquid state. Acetonitrile contains molecules with strong parallel and antiparallel orientations and this strongly ordered structure is stabilized by dipole–dipole interactions [10], where as 2-alkanols are associated through the hydrogen bonding of their hydroxyl groups.

Molecular association decreases with increase in chain-length of 2-alkanol. The increase in V_m^E with the increase in chain-length of 2-alkanol implies that acetonitrile-2-alkanol interaction is relatively

Table 3
Densities ρ, viscosities η, refractive indices n_D, of mixing for the binary mixtures as a function of the mole fraction x_1 of acetonitrile.

x_1	ρ (g cm^{-3})	$\bar{V}_{m,1}$ (cm^3 mol^{-1})	$\bar{V}_{m,2}$ (cm^3 mol^{-1})	η (mPa s)	n_D
Acetonitrile(1) + 2-propanol (2) at 293.15 K					
0.0000	0.78519			2.3511	1.3766
0.0496	0.78497	52.771	76.534	1.9715	1.3757
0.0906	0.78472	52.88	76.527	1.6877	1.3751
0.1529	0.78431	52.943	76.514	1.3682	1.3737
0.2022	0.78390	52.944	76.517	1.1759	1.3726
0.2783	0.78336	52.888	76.531	0.9608	1.3705
0.3678	0.78271	52.801	76.575	0.7912	1.3677
0.4768	0.78202	52.713	76.65	0.6502	1.3640
0.6132	0.78153	52.636	76.726	0.5100	1.3590
0.7714	0.78113	52.578	76.858	0.4156	1.3528
0.9207	0.78126	52.517	77.272	0.3716	1.3469
1.0000	0.78204			0.3542	1.3436
At 298.15 K					
0.0000	0.78098			2.0439	1.3745
0.0496	0.78076	53.258	76.937	1.6909	1.3733
0.0906	0.7803	53.394	76.939	1.4612	1.3724
0.1529	0.7797	53.468	76.929	1.2074	1.3713
0.2022	0.7797	53.460	76.93	1.044	1.3702
0.2783	0.7792	53.374	76.945	0.8677	1.3687
0.3678	0.77765	53.254	77.009	0.7248	1.3667
0.4768	0.77879	53.126	77.121	0.6062	1.3635
0.6132	0.77620	53.006	77.239	0.4735	1.3591
0.7714	0.77579	52.935	77.403	0.3840	1.3528
0.9207	0.77595	52.878	77.774	0.3499	1.3452
1.0000	0.77664			0.3369	1.3411
At 303.15 K					
0.0000	0.77671			1.7583	1.3724
0.0496	0.77632	53.7846	77.3646	1.4742	1.3715
0.0906	0.77584	53.8653	77.3658	1.2875	1.3707
0.1529	0.77513	53.8919	77.3638	1.0692	1.3694
0.2022	0.77454	53.8646	77.3722	0.9367	1.3684
0.2783	0.77397	53.7647	77.3918	0.7975	1.3666
0.3678	0.77288	53.6389	77.4536	0.6615	1.3641
0.4768	0.77184	53.5155	77.5639	0.5492	1.3608
0.6132	0.77113	53.3939	77.684	0.4429	1.3561
0.7714	0.77052	53.3163	77.8716	0.3617	1.3500
0.9207	0.77059	53.2502	78.2738	0.3311	1.3433
1.0000	0.77121			0.3254	1.3390
At 308.15 K					
0.0000	0.77236			1.5315	1.3703
0.0496	0.77186	54.224	77.8059	1.2958	1.3694
0.0906	0.77131	54.3317	77.8052	1.1500	1.3687
0.1529	0.77057	54.3794	77.7908	0.9576	1.3679
0.2022	0.76992	54.3607	77.792	0.8460	1.3670
0.2783	0.76898	54.2652	77.8124	0.7168	1.3657
0.3678	0.76780	54.1254	77.8884	0.6057	1.3637
0.4768	0.76644	53.9689	78.0409	0.5051	1.3605
0.6132	0.76575	53.7788	78.2157	0.4111	1.3557
0.7714	0.76526	53.6666	78.4583	0.3442	1.3491
0.9207	0.76518	53.6311	78.7756	0.3202	1.3417
1.0000	0.76575			0.3082	1.3371
Acetonitrile(1) + 2-buanol (2) at 293.15 K					
0.0000	0.80657			3.9119	1.3966
0.0844	0.80453	53.459	91.909	2.5031	1.3952
0.1644	0.8025	53.263	91.951	1.6545	1.3930
0.2516	0.80041	53.153	91.981	1.3764	1.3899
0.3369	0.79833	53.066	92.013	1.0890	1.3860
0.4444	0.79568	52.922	92.096	0.8564	1.3804
0.5382	0.79335	52.767	92.241	0.6953	1.3751
0.6425	0.7907	52.613	92.498	0.5565	1.3686
0.7610	0.7881	52.487	92.791	0.4636	1.3610
0.8715	0.78592	52.452	92.845	0.3984	1.3534
0.9588	0.78348	52.488	92.513	0.3663	1.3467
1.0000	0.78204			0.3542	1.3436
At 298.15 K					
0.0000	0.80256			3.1318	1.3946
0.0844	0.80028	54.045	92.369	2.1353	1.3918
0.1644	0.79807	53.784	92.417	1.5742	1.3893
0.2516	0.79579	53.582	92.474	1.2185	1.3865
0.3369	0.79363	53.431	92.532	0.9920	1.3830
0.4444	0.79096	53.268	92.621	0.7937	1.3782

Table 3 (*Continued*)

x_1	ρ (g cm^{-3})	$\bar{V}_{m,1}$ (cm^3 mol^{-1})	$\bar{V}_{m,2}$ (cm^3 mol^{-1})	η (mPa s)	n_D
0.5382	0.7885	53.152	92.738	0.6498	1.3734
0.6425	0.78567	53.045	92.919	0.5180	1.3674
0.7610	0.78265	52.938	93.164	0.4216	1.3597
0.8715	0.77999	52.871	93.405	0.3868	1.3518
0.9588	0.77771	52.861	93.581	0.3632	1.3448
1.0000	0.77664			0.3369	1.3411
At 303.15 K					
0.0000	0.79826			2.5340	1.3924
0.0844	0.79595	54.407	92.865	1.7943	1.3902
0.1644	0.79374	54.216	92.893	1.3829	1.3886
0.2516	0.79138	54.012	92.945	1.0822	1.3860
0.3369	0.78907	53.837	93.018	0.8873	1.3829
0.4444	0.78617	53.66	93.131	0.7129	1.3779
0.5382	0.78362	53.544	93.245	0.5936	1.3722
0.6425	0.78073	53.444	93.393	0.4865	1.3656
0.7610	0.77745	53.347	93.613	0.4019	1.3575
0.8715	0.77443	53.271	93.943	0.3612	1.3495
0.9588	0.77205	53.244	93.374	0.3414	1.3426
1.0000	0.77121			0.3254	1.3390
At 308.15 K					
0.0000	0.79396			2.1723	1.3905
0.0844	0.79155	54.855	93.368	1.5718	1.3876
0.1644	0.78927	54.669	93.391	1.2127	1.3853
0.2516	0.78677	54.446	93.45	0.9642	1.3825
0.3369	0.78437	54.246	93.53	0.8021	1.3799
0.4444	0.78135	54.052	93.657	0.6524	1.3753
0.5382	0.77869	53.935	93.774	0.5479	1.3713
0.6425	0.77568	53.841	93.912	0.4533	1.3659
0.7610	0.77227	53.743	94.119	0.3790	1.3592
0.8715	0.76899	53.665	94.493	0.3437	1.3510
0.9588	0.76651	53.628	95.049	0.3238	1.3423
1.0000	0.76575			0.3082	1.3371
Acetonitrile(1) + 2-pentanol (2) at 293.15 K					
0.0000	0.80929			4.2982	1.4060
0.1160	0.80675	53.427	108.933	2.5440	1.4035
0.1727	0.80546	53.342	108.946	2.0931	1.4020
0.2827	0.80279	53.181	109	1.5337	1.3981
0.3546	0.80101	53.072	109.049	1.2618	1.3951
0.4458	0.79866	52.94	109.136	1.0078	1.3908
0.5366	0.79626	52.815	109.249	0.8100	1.3858
0.6488	0.79309	52.689	109.438	0.6391	1.3779
0.7671	0.78952	52.589	109.7	0.5048	1.3674
0.8793	0.78603	52.522	110.002	0.4119	1.3561
0.9578	0.78359	52.489	110.244	0.3705	1.3478
1.0000	0.78204			0.3542	1.3436
At 298.15 K					
0.0000	0.80524			3.4785	1.4045
0.1160	0.80261	53.783	109.485	2.1703	1.4012
0.1727	0.80125	53.699	109.502	1.8045	1.3999
0.2827	0.79855	53.553	109.543	1.3619	1.3965
0.3546	0.79668	53.462	109.586	1.1248	1.3941
0.4458	0.79417	53.343	109.669	0.9044	1.3901
0.5366	0.7916	53.217	109.787	0.7392	1.3848
0.6488	0.78828	53.069	109.997	0.5884	1.3764
0.7671	0.78454	52.952	110.301	0.4715	1.3657
0.8793	0.78088	52.883	110.621	0.3910	1.3548
0.9578	0.77828	52.855	110.82	0.3537	1.3461
1.0000	0.77664			0.3369	1.3411
At 303.15 K					
0.0000	0.77671			1.7583	1.3724
0.1160	0.77632	53.784	77.364	1.4742	1.3715
0.1727	0.77584	53.865	77.365	1.2875	1.3707
0.2827	0.77513	53.891	77.363	1.0692	1.3694
0.3546	0.77454	53.864	77.372	0.9367	1.3684
0.4458	0.77397	53.764	77.391	0.7975	1.3666
0.5366	0.77288	53.638	77.453	0.6615	1.3641
0.6488	0.77184	53.515	77.563	0.5492	1.3608
0.7671	0.77113	53.393	77.684	0.4429	1.3561
0.8793	0.77052	53.316	77.871	0.3617	1.3500
0.9578	0.77059	53.25	78.273	0.3311	1.3433
1.0000	0.77121			0.3254	1.3390

Table 3 (*Continued*)

x_1	ρ (g cm^{-3})	$\bar{V}_{m,1}$ (cm^3 mol^{-1})	$\bar{V}_{m,2}$ (cm^3 mol^{-1})	η (mPa s)	n_D
308.15 K					
0.0000	0.77236			1.5315	1.3703
0.1160	0.77186	54.224	77.805	1.2958	1.3694
0.1727	0.77131	54.331	77.805	1.1500	1.3687
0.2827	0.77057	54.379	77.79	0.9576	1.3679
0.3546	0.76992	54.36	77.792	0.8460	1.3670
0.4458	0.76898	54.265	77.812	0.7168	1.3657
0.5366	0.76780	54.125	77.888	0.6057	1.3637
0.6488	0.76644	53.968	78.04	0.5051	1.3605
0.7671	0.76575	53.778	78.215	0.4111	1.3557
0.8793	0.76526	53.666	78.458	0.3442	1.3491
0.9578	0.76518	53.631	78.775	0.3202	1.3417
1.0000	0.76575			0.3082	1.3371
Acetonitrile(1) + 2-hexanol (2) at 293.15 K					
0.0000	0.81408			5.1550	1.4135
0.0964	0.81214	53.387	125.599	3.4907	1.4103
0.1813	0.81022	53.362	125.603	2.6962	1.4077
0.2574	0.80834	53.289	125.626	2.1277	1.4051
0.3436	0.80607	53.167	125.678	1.6839	1.4014
0.4483	0.80311	52.997	125.789	1.2763	1.3972
0.5398	0.80033	52.851	125.934	1.0062	1.3917
0.6495	0.79676	52.698	126.157	0.7676	1.3837
0.7580	0.79288	52.587	126.421	0.5820	1.3739
0.8733	0.7819	52.519	126.73	0.4444	1.3621
0.9579	0.78429	52.494	126.949	0.3758	1.3510
1.0000	0.78204			0.3542	1.3436
At 298.15 K					
0.0000	0.81014			4.100	1.4116
0.0964	0.80814	53.769	126.208	2.9326	1.4096
0.1813	0.80614	53.756	126.211	2.2839	1.4078
0.2574	0.80419	53.685	126.233	1.8402	1.4054
0.3436	0.80182	53.561	126.286	1.4749	1.4022
0.4483	0.79872	53.384	126.402	1.1327	1.3975
0.5398	0.79582	53.231	126.552	0.9062	1.3924
0.6495	0.79209	53.072	126.785	0.6995	1.3837
0.7580	0.78802	52.956	127.061	0.5384	1.3730
0.8733	0.78308	52.887	127.383	0.4184	1.3595
0.9579	0.77902	52.857	127.611	0.3583	1.3480
1.0000	0.77664			0.336	1.3411
At 303.15 K					
0.0000	0.80613			3.41	1.4093
0.0964	0.80404	54.216	126.833	2.4914	1.4082
0.1813	0.80194	54.181	126.84	1.9671	1.4064
0.2574	0.79991	54.068	126.874	1.6100	1.4044
0.3436	0.79749	53.908	126.942	1.3014	1.4021
0.4483	0.79438	53.719	127.057	1.0167	1.3979
0.5398	0.79133	53.599	127.193	0.82121	1.3925
0.6495	0.78745	53.475	127.364	0.6409	1.3839
0.7580	0.78307	53.376	127.594	0.5036	1.3740
0.8733	0.77774	53.286	128.011	0.3943	1.3596
0.9579	0.77337	53.243	128.55	0.3411	1.3450
1.0000	0.77121			0.325	1.3390
At 308.15 K					
0.0000	0.80206			2.819	1.4077
0.0964	0.79997	54.552	127.472	2.1336	1.4069
0.1813	0.79784	54.589	127.464	1.7084	1.4061
0.2574	0.79574	54.499	127.488	1.4198	1.4049
0.3436	0.79318	54.337	127.559	1.1548	1.4026
0.4483	0.78988	54.126	127.7	0.9154	1.3979
0.5398	0.78673	53.974	127.864	0.7511	1.3925
0.6495	0.78283	53.817	128.064	0.5933	1.3844
0.7580	0.77836	53.719	128.305	0.4724	1.3745
0.8733	0.77284	53.65	128.638	0.3759	1.3610
0.9579	0.76823	53.618	128.996	0.3263	1.3469
1.0000	0.76575			0.308	1.3371
Acetonitrile(1) + 2-heptanol (2) at 293.15 K					
0.0000	0.81718			6.5198	1.4206
0.1142	0.81497	53.429	142.194	4.3265	1.417
0.1947	0.81316	53.378	142.205	3.3365	1.4145
0.2510	0.81178	53.304	142.231	2.7697	1.4124
0.3491	0.80924	53.144	142.301	2.1331	1.4094
0.4525	0.80632	52.98	142.407	1.5843	1.4042
0.5436	0.80352	52.854	142.519	1.2387	1.3986

Table 3 (*Continued*).

x_1	ρ (g cm^{-3})	$\bar{V}_{m,1}$ (cm^3 mol^{-1})	$\bar{V}_{m,2}$ (cm^3 mol^{-1})	η (mPa s)	n_D
0.6702	0.7989	52.726	142.732	0.8636	1.3881
0.7574	0.79518	52.651	142.938	0.6732	1.3793
0.8770	0.78927	52.551	142.392	0.5444	1.3637
0.9588	0.78477	52.492	142.907	0.3857	1.3516
1.0000	0.78204			0.3542	1.3436
At 298.15 K					
0.0000	0.81333			5.3303	1.4188
0.1142	0.81107	53.847	142.857	3.5832	1.4158
0.1947	0.80919	53.825	142.859	2.8206	1.4146
0.2510	0.80774	53.74	142.887	2.4016	1.4129
0.3491	0.80500	53.546	142.985	1.8531	1.4094
0.4525	0.80207	53.330	143.106	1.3949	1.4039
0.5436	0.79912	53.197	143.241	1.1061	1.3979
0.6702	0.79443	53.072	143.436	0.7855	1.3873
0.7574	0.79057	53.009	143.611	0.6191	1.3781
0.8770	0.78426	52.925	144.038	0.5120	1.3629
0.9588	0.77964	52.85	144.569	0.3652	1.3503
1.0000	0.77664			0.3369	1.3411
At 303.15 K					
0.0000	0.80944			4.3006	1.4165
0.1142	0.80706	54.218	143.553	3.0302	1.4134
0.1947	0.80514	54.171	143.557	2.4092	1.4127
0.2510	0.80362	54.1	143.59	2.0664	1.4118
0.3491	0.80093	53.911	143.663	1.6188	1.4093
0.4525	0.79779	53.716	143.791	1.2505	1.4029
0.5436	0.79469	53.587	143.939	0.9893	1.3973
0.6702	0.78988	53.424	144.167	0.7174	1.3863
0.7574	0.78600	53.346	144.356	0.5762	1.3774
0.8770	0.77950	53.275	144.724	0.4829	1.3620
0.9588	0.77436	53.231	145.088	0.3483	1.3481
1.0000	0.77121			0.3254	1.3390
At 308.15 K					
0.0000	0.80550			3.5285	1.4143
0.1142	0.80317	54.694	144.22	2.5779	1.4156
0.1947	0.80112	54.762	144.202	2.072	1.4141
0.2510	0.79949	54.667	144.237	1.8160	1.4126
0.3491	0.79653	54.384	144.363	1.4660	1.4079
0.4525	0.79331	54.09	144.546	1.1116	1.4022
0.5436	0.79011	53.93	144.724	0.8985	1.3958
0.6702	0.78523	53.801	144.896	0.6625	1.3845
0.7574	0.78116	53.751	145.018	0.5390	1.3744
0.8770	0.77415	53.687	145.41	0.4454	1.3576
0.9588	0.76893	53.61	146.029	0.3326	1.3452
1.0000	0.76575			0.3082	1.3371

weaker. Assuming the positive contribution due to H-bond breaking to be constant, the observed increase in V_m^E with increase in chain-length of 2-alkanol can be rationalized.

The positive V_m^E values for mixtures of acetonitrile with 2-alkanol can be ascribed to dominance of disruption of H-bonds between alkanols over dipole–dipole interactions between 2-alkanols and acetonitrile molecule.

Its be mentioned that V_m^E values for mixtures of acetonitrile with 1-alkanol also are positive and increase with increasing chain-length of 1-alkanols [13]. But difference in V_m^E between 2-alkanols and 1-alkanols are dependent on the position of the –OH group in the alkanol molecules.

The partial molar volumes $\bar{V}_{m,i}$, in these mixtures were calculated over the whole composition range using Eqs. (4) and (5) [11,12].

$$\bar{V}_{m,1} = V_m^E + V_{m,1}^* + (1-x)\left(\frac{\partial V_m^E}{\partial x}\right)_{T,P} \quad (5)$$

$$\bar{V}_{m,2} = V_m^E + V_{m,2}^* - x\left(\frac{\partial V_m^E}{\partial x}\right)_{T,P} \quad (6)$$

Table 4
Partial molar volumes at infinite dilution $\bar{V}_{m,i}^o$, for acetonitrile + 2-alkanols at different temperatures.

	293.15 K	298.15 K	303.15 K	308.15 K
Acetonitrile (1) + 2-propanol (2)				
$\bar{V}_{m,1}^o$ (cm^3 mol^{-1})	52.947	53.479	53.938	54.439
$\bar{V}_{m,2}^o$ (cm^3 mol^{-1})	77.11	77.657	78.146	78.706
Acetonitrile (1) + 2-butanol (2)				
$\bar{V}_{m,1}^o$ (cm^3 mol^{-1})	53.458	53.954	54.361	54.807
$\bar{V}_{m,2}^o$ (cm^3 mol^{-1})	92.813	93.51	94.121	94.712
Acetonitrile (1) + 2-pentanol (2)				
$\bar{V}_{m,1}^o$ (cm^3 mol^{-1})	53.499	53.874	54.328	54.739
$\bar{V}_{m,2}^o$ (cm^3 mol^{-1})	110.11	110.704	111.32	111.948
Acetonitrile (1) + 2-hexanol (2)				
$\bar{V}_{m,1}^o$ (cm^3 mol^{-1})	53.537	53.935	54.335	54.740
$\bar{V}_{m,2}^o$ (cm^3 mol^{-1})	126.838	127.493	128.209	128.808
Acetonitrile (1) + 2-heptanol (2)				
$\bar{V}_{m,1}^o$ (cm^3 mol^{-1})	53.56	53.994	54.359	54.904
$\bar{V}_{m,2}^o$ (cm^3 mol^{-1})	143.695	144.241	144.885	145.695

where $V_{m,1}^*$ and $V_{m,2}^*$ are pure molar volumes of component 1, 2 respectively. Values of partial molar volumes $\bar{V}_{m,i}$ are given in Table 3 and partial molar volumes at infinite dilution $\bar{V}_{m,i}^o$, are in Table 4.

The partial properties at infinite dilution are of interest since at the limit of infinite dilution the solute–solute interactions disappear and only interactions present are solute–solvent interactions. Since the partial molar volumes at infinite dilution of each component, are not very different from the corresponding molar volumes $V_{m,i}^*$, interaction between acetonitrile and alcohols is not very favorable. $\bar{V}_{m,i}^o$ increases with chain-length of alkanols and slightly increase with temperature.

3.2. Theoretical analysis

The Flory's theory [14–18] and its extended forms [19–22] have been used extensively to predict excess properties of non-electrolyte systems for different kinds of mixtures, including polar components [23–25]. The present work reports the applicability of the Prigogine–Flory–Patterson theory (PFP theory) to predict excess molar volume of binary mixtures of 2-alkanols with acetonitrile.

According to the PFP theory, V_m^E, calculations include three contributions: (i) interactional, which is proportional to the (χ_{12}) parameters; (ii) the free volume contribution which arises from the dependence of the reduced volume upon the reduced temperature as a result of the difference between the degree of expansion of the two components and (iii) the (P^*) contribution, which depends both on the differences of internal pressures and differences of reduced volumes of the components. The V_m^E was calculated by means of the PFP theory using the following equation with the three contributions.

$$\frac{V_m^E}{(x_1 V_1^* x_2 V_2^*)} = \left(\frac{(\tilde{V}^{1/3} - 1)\tilde{V}^{1/3}\varphi_1\theta_2\chi_{12}}{((4/3)\tilde{V}^{1/3} - 1)P_1^*} \right)(x_1 V_1^* + x_2 V_2^*)$$

$$- \frac{(\tilde{V}_1 - \tilde{V}_2)^2((14/9)\tilde{V}^{-1/3} - 1)\psi_1\psi_2}{((4/3)\tilde{V}^{1/3} - 1)\tilde{V}}(x_1 V_1^* + x_2 V_2^*)$$

$$+ \frac{(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)\psi_1\psi_2}{P_1^*\varphi_2 - P_2^*\varphi_2}(x_1 V_1^* + x_2 V_2^*); \qquad (7)$$

The $\tilde{V}$ of the solution is obtained through the Flory's theory. The characteristic parameters V^* and P^* are obtained from thermal expansion coefficient, (α_P) and isothermal compressibility (β_T). The thermal expansion coefficient (α_i) is used to calculate the reduced volume by equation:

$$\tilde{V}_i = \left(\frac{1 + (4/3)\alpha_i T}{1 + \alpha_i T} \right)^3; \qquad (8)$$

Here, the molecular contact energy fraction is calculated by:

$$\psi_1 = \frac{\varphi_1 P_1^*}{\varphi_1 P_1^* + \varphi_2 P_2^*} \qquad (9)$$

Table 5
Parameters of pure components used in Flory theory at 298.15 K.

Component	P^* (J cm^{-3})	V^* (cm^3 mol^{-1})	T^* (K)
Acetonitrile	456.106	41.6273	4946.39
2-Propanol	479.031	60.593	5163.6
2-Butanol	347.579	72.7335	5947.78
2-Pentanol	190.82	86.2095	5396.01
2-Hexanol	210.706	99.3931	5269.12
2-Heptanol	231.155	112.515	5279.53

with the hard-core volume fractions defined by:

$$\varphi_1 = \frac{x_1 V_1^*}{x_1 V_1^* + x_2 V_2^*} \qquad (10)$$

The molecular surface fraction is calculated by:

$$\theta_2 = \frac{\varphi_2 S_2}{\varphi_2 S_2 + \varphi_1 S_1} \qquad (11)$$

where S_i is the molecular fraction surface/volume ratio for the components determined by Bondi's method [26].

The values of pure parameters for the pure liquid components and the mixture are obtained by Flory theory [14]. The parameters for the pure liquid components derived using Flory theory are in Table 5.

The values of thermal expansion coefficient and isothermal compressibility for the pure components obtained from the literature. In order to obtain V_m^E, it is necessary to find the interactional parameter (χ_{12}) which was obtained by fitting the theory to experimental values of V_m^E for each one of the binary system. Table 6 presents the calculated equimolar values of the three contributions to V_m^E according to Eq. (7), together with the interactional parameter (χ_{12}). An analysis of each of the three contributions to V_m^E shows that the interactional contribution is always positive in all binary mixtures of acetonitrile and 2-alkanol. The free volume effect, is negative and it seems to have little significance for the system studied. The third contribution due to different in internal pressure and in reduced volume of the components seems to be the most important to explain the V_m^E behavior, except 2-propanol for system studied. Figs. 2–6 show the excess molar values predicted by PFP theory for acetonitrile and 2-alkanols systems.

3.3. Dynamic viscosities

The viscosity deviation can be calculated as

$$\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2 \qquad (12)$$

where η is the viscosity of mixture and η_1 and η_2 are pure components viscosity. The measured η values for binary systems at different temperatures are listed in Table 3.

The $\Delta\eta$ values were fitted to Redlich–Kister equation (3) and the adjustable parameters and standard deviations are given in Table 2.

The viscosity deviation represents deviations from a rectilinear dependence of viscosity on mole fraction. The values of $\Delta\eta$ that shown in Fig. 7, for the system containing 2-alkanols + acetonitrile, were asymmetrical and all negative throughout the whole concentration range at all the temperatures, with the more negative as the length of the alkanol chain increase.

Table 6
Calculated values of three contributions of the PFP theory to V_m^E for (2-alkanols + acetonitrile) mixtures at 298.15 K.

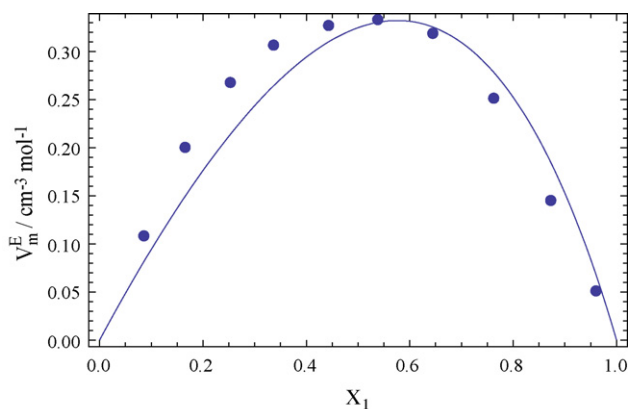| System	χ_{12} (J cm^{-3})	Interactional	Free volume	P^*
x_1 [acetonitrile] + (1 − x_1) 2-propanol	23	0.2622	−0.0054	−0.0104
x_1 [acetonitrile] + (1 − x_1) 2-butanol	19.2	0.1798	−0.0864	0.2350
x_1 [acetonitrile] + (1 − x_1) 2-pentanol	2.4	0.02650	−0.0257	0.3764
x_1 [acetonitrile] + (1 − x_1) 2-hexanol	8.3	0.0963	−0.0158	0.2779
x_1 [acetonitrile] + (1 − x_1) 2-heptanol	8.6	0.0995	−0.0181	0.2734

Fig. 3. Plot of excess molar volume V_m^E against mole fraction of acetonitrile for the $\{x_1 \text{ acetonitrile} + (1 - x_1) \text{ 2-butanol}\}$ mixtures. (●) Experimental; (– –) calculated by using PFP theory.
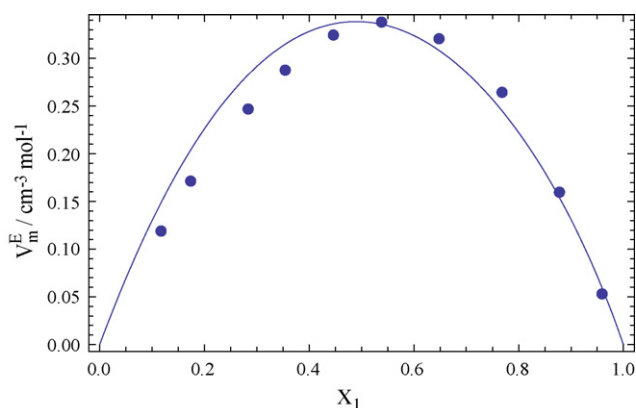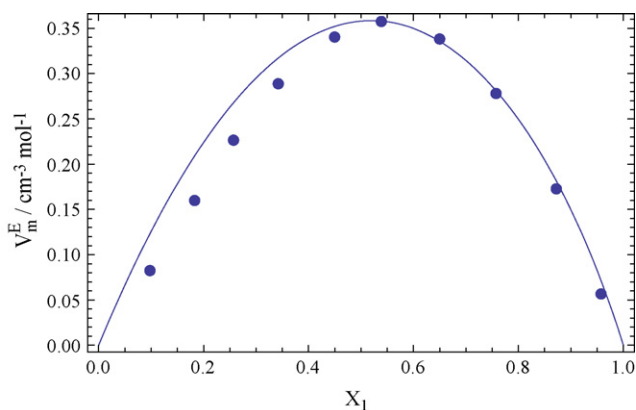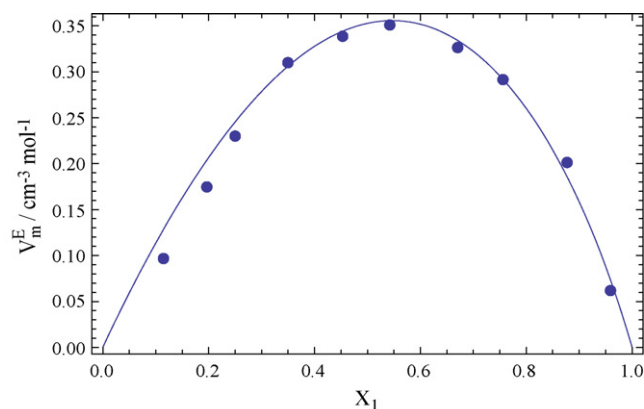

Fig. 6. Plot of excess molar volume V_m^E against mole fraction of acetonitrile for the $\{x_1 \text{ acetonitrile} + (1 - x_1) \text{ 2-heptanol}\}$ mixtures. (●) Experimental; (– –) calculated by using PFP theory.

Fig. 4. Plot of excess molar volume V_m^E against mole fraction of acetonitrile for the $\{x_1 \text{ acetonitrile} + (1 - x) \text{ 2-pentanol}\}$ mixtures. (●) Experimental; (– –) calculated by using PFP theory.
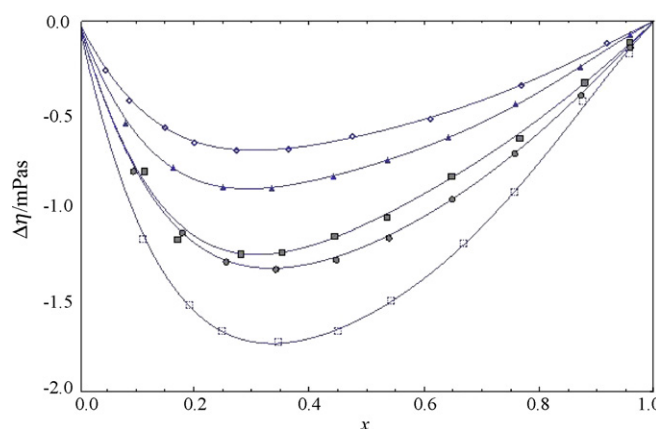

Fig. 7. Viscosity deviations of binary mixtures for acetonitrile with (◇) 2-propanol, (▲) 2-butanol, (■) 2-pentanol, (●) 2-hexanol, (□) 2-heptanol at 298.15 K.

The negative values of viscosity deviations for the binary systems investigated suggest that the viscosities of associates formed between unlike molecules are relatively less than those of the pure components. Also there are some reports on viscosity of acetonitrile + 1-alkanol [2,13]. Similar to 1-alkanol + acetonitrile mixtures, the values of viscosity deviation for 2-alkanols + acetonitrile also increase with the chain-length of 2-alkanols. However, the values of viscosity deviation for 1-alkanol mixtures are significantly higher

than those mixtures involving the corresponding 2-alkanols. Thus, the values of viscosity deviation are dependent on the position of the –OH group in the alkanol molecules.

Interaction between acetonitrile and 2 alkanols is said to involve a weak bond intermediate between a hydrogen bond and formation of an electron transfer complex. There is evidence for weak complex formation between acetonitrile and 2-alkanols.
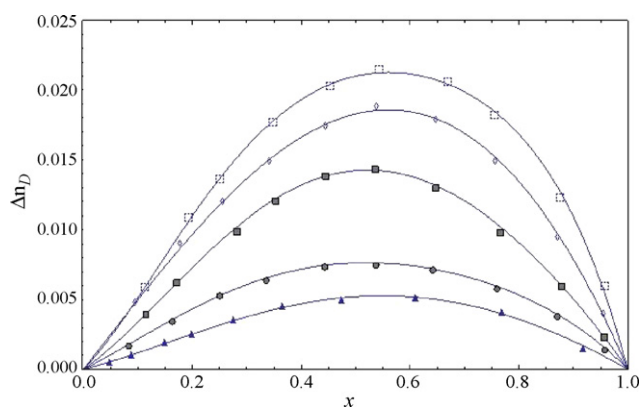

Fig. 5. Plot of excess molar volume V_m^E against mole fraction of acetonitrile for the $\{x_1 \text{ acetonitrile} + (1 - x_1) \text{ 2-hexanol}\}$ mixtures. (●) Experimental; (– –) calculated by using PFP theory.

Fig. 8. Refractive index deviations on mixing of acetonitrile with (▲) 2-propanol, (●) 2-butanol, (■) 2-pentanol, (◇) 2-hexanol, (□) 2-heptanol at 298.15 K. Solid lines represent the Redlich–Kister fit.

3.4. Refractive index

Refractive index deviations were defined by

$$\Delta n_D = n_D - \{x n_{D,1}^* + (1-x) n_{D,2}^*\} \tag{13}$$

where n_D is the refractive index of the mixture, $n_{D,i}^*$ is that corresponding to the pure component i and x is the mole fraction of component 1 in the mixture. The experimental refractive indices of the binary mixtures at different temperatures are listed in Table 3, and the values of Δn_D are shown in Fig. 8. The results were fitted by Eq. (3) and the adjustable parameters and standard deviations are given in Table 2.

It can be seen that the changes in refractive index of all 2-alkanol mixtures with acetonitrile are positive throughout the entire composition range, while the chain-length of the 2-alkanol increases the change in the refractive index becomes more positive. The same can be said about the change in refractive index of these mixtures at higher temperatures which were slightly more positive than they were at 293.15 K.

Fig. 8 shows that the maximum of refractive index deviations occur at equimolar concentration of acetonitrile with 2-alkanols, and becomes grater as temperature increases.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2009.06.015.

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