Thermochimica Acta 495 (2009) 139–148

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

# 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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ARTICLE INFO

*Article history:*
Received 18 March 2009
Received in revised form 3 June 2009
Accepted 10 June 2009
Available online 18 June 2009

*Keywords:*
Density
Viscosity
Excess molar volumes
Refractive index
Acetonitrile
2-Alkanols
Redlich–Kister equation
PFP theory

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 $\Delta n_D$ 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.


## 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

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

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doi:10.1016/j.tca.2009.06.015

**Table 1**
Experimental and literature values of densities $\rho$, viscosities $\eta$, and refractive indices $n_D$, of acetonitrile, 2-propanol, 2-butanol, 2-pentanol, 2-hexanol and 2-heptanol at 298.15 K.

| Compound | $\rho$ (g cm$^{-3}$) | | $\eta$ (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 $\eta$ 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 $\pm 0.01$ K.

Refractive indices were measured using a high accuracy Abbe refractometer with an accuracy of $\pm 4 \times 10^{-5}$. 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 $\pm 1 \times 10^{-4}$.

## 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

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

where $\rho$ is the density of the mixture, $\rho_i$ 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

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

where $Y^E \equiv V_m^E$ or $\Delta\eta$ or $\Delta n_D$ 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 $\sigma$ with

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

where $Y_{\text{exp.}}$ and $Y_{\text{cal.}}$ 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 $\sigma$. 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

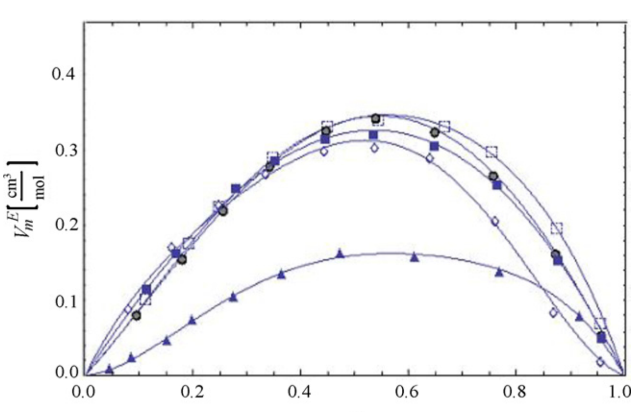


**Fig. 1.** Excess molar volumes $V_m^E$ vs. mole fraction of acetonitrile for acetonitrile binary mixtures with (▲) 2-propanol, (◇) 2-butanol, (■) 2-pentanol, (●) 2-hexanol, (□) 2-heptanol at 298.15 K. The solid curves were calculated from coefficients of Eq. (3) given in Table 2.

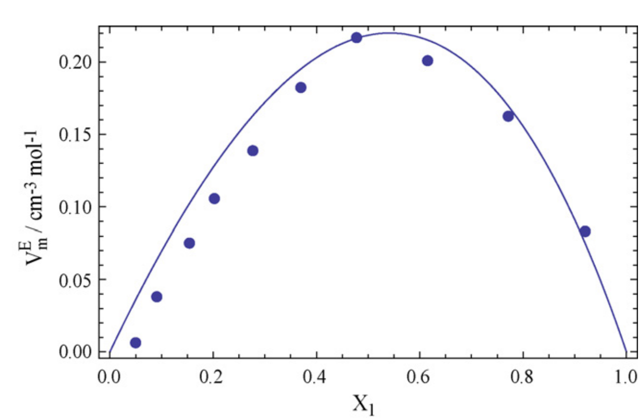


**Fig. 2.** Plot of excess molar volume $V_m^E$ against mole fraction of acetonitrile for the {$x_1$ acetonitrile + $(1-x_1)$ 2-propanol} mixtures. (●) Experimental; (– –) calculated by using PFP theory.

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

| | | Temperature | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $\sigma$ |
|---|---|---|---|---|---|---|---|
| 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 |
| | $\Delta n_D$ | 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 |
| | $\Delta n_D$ | 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 |
| | $\Delta n_D$ | 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 |
| | $\Delta n_D$ | 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 |
| | $\Delta n_D$ | 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 $\rho$, viscosities $\eta$, refractive indices $n_D$, of mixing for the binary mixtures as a function of the mole fraction $x_1$ of acetonitrile.

| $x_1$ | $\rho$ (g cm$^{-3}$) | $\bar{V}_{m,1}$ (cm$^3$ mol$^{-1}$) | $\bar{V}_{m,2}$ (cm$^3$ mol$^{-1}$) | $\eta$ (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* )

| $x_1$ | $\rho$ (g cm$^{-3}$) | $\bar{V}_{m,1}$ (cm$^3$ mol$^{-1}$) | $\bar{V}_{m,2}$ (cm$^3$ mol$^{-1}$) | $\eta$ (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* )

| $x_1$ | $\rho$ (g cm$^{-3}$) | $\bar{V}_{m,1}$ (cm$^3$ mol$^{-1}$) | $\bar{V}_{m,2}$ (cm$^3$ mol$^{-1}$) | $\eta$ (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* ).

| $x_1$ | $\rho$ (g cm$^{-3}$) | $\bar{V}_{m,1}$ (cm$^3$ mol$^{-1}$) | $\bar{V}_{m,2}$ (cm$^3$ mol$^{-1}$) | $\eta$ (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].

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

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

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

| | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
|---|---|---|---|---|
| Acetonitrile (1) + 2-propanol (2) | | | | |
| $\overline{V}_{m,1}^{o}$ (cm$^3$ mol$^{-1}$) | 52.947 | 53.479 | 53.938 | 54.439 |
| $\overline{V}_{m,2}^{o}$ (cm$^3$ mol$^{-1}$) | 77.11 | 77.657 | 78.146 | 78.706 |
| Acetonitrile (1) + 2-butanol (2) | | | | |
| $\overline{V}_{m,1}^{o}$ (cm$^3$ mol$^{-1}$) | 53.458 | 53.954 | 54.361 | 54.807 |
| $\overline{V}_{m,2}^{o}$ (cm$^3$ mol$^{-1}$) | 92.813 | 93.51 | 94.121 | 94.712 |
| Acetonitrile (1) + 2-pentanol (2) | | | | |
| $\overline{V}_{m,1}^{o}$ (cm$^3$ mol$^{-1}$) | 53.499 | 53.874 | 54.328 | 54.739 |
| $\overline{V}_{m,2}^{o}$ (cm$^3$ mol$^{-1}$) | 110.11 | 110.704 | 111.32 | 111.948 |
| Acetonitrile (1) + 2-hexanol (2) | | | | |
| $\overline{V}_{m,1}^{o}$ (cm$^3$ mol$^{-1}$) | 53.537 | 53.935 | 54.335 | 54.740 |
| $\overline{V}_{m,2}^{o}$ (cm$^3$ mol$^{-1}$) | 126.838 | 127.493 | 128.209 | 128.808 |
| Acetonitrile (1) + 2-heptanol (2) | | | | |
| $\overline{V}_{m,1}^{o}$ (cm$^3$ mol$^{-1}$) | 53.56 | 53.994 | 54.359 | 54.904 |
| $\overline{V}_{m,2}^{o}$ (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 $\overline{V}^o_{m,i}$, 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. $\overline{V}^o_{m,i}$ 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, $V^E_m$, calculations include three contributions: (i) interactional, which is proportional to the $(\chi_{12})$ 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 $V^E_m$ was calculated by means of the PFP theory using the following equation with the three contributions.

$$\frac{V^E_m}{(x_1V^*_1x_2V^*_2)} = \left(\frac{(\tilde{V}^{1/3}-1)\tilde{V}^{1/3}\varphi_1\theta_2\chi_{12}}{((4/3)\tilde{V}^{1/3}-1)P^*_1}\right)(x_1V^*_1+x_2V^*_2) - \frac{(\tilde{V}_1-\tilde{V}_2)^2((14/9)\tilde{V}^{-1/3}-1)\psi_1\psi_2}{((4/3)\tilde{V}^{1/3}-1)\tilde{V}}(x_1V^*_1+x_2V^*_2) + \frac{(\tilde{V}_1-\tilde{V}_2)(P^*_1-P^*_2)\psi_1\psi_2}{P^*_1\varphi_2-P^*_2\varphi_2}(x_1V^*_1+x_2V^*_2); \tag{7}$$

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, $(\alpha_P)$ and isothermal compressibility $(\beta_T)$. The thermal expansion coefficient $(\alpha_i)$ is used to calculate the reduced volume by equation:

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

Here, the molecular contact energy fraction is calculated by:

$$\psi_1 = \frac{\varphi_1P^*_1}{\varphi_1P^*_1+\varphi_2P^*_2} \tag{9}$$

**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:

$$\varphi_1 = \frac{x_1V^*_1}{x_1V^*_1+x_2V^*_2} \tag{10}$$

The molecular surface fraction is calculated by:

$$\theta_2 = \frac{\varphi_2S_2}{\varphi_2S_2+\varphi_1S_1} \tag{11}$$

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 $V^E_m$, it is necessary to find the interactional parameter $(\chi_{12})$ which was obtained by fitting the theory to experimental values of $V^E_m$ for each one of the binary system. Table 6 presents the calculated equimolar values of the three contributions to $V^E_m$ according to Eq. (7), together with the interactional parameter $(\chi_{12})$. An analysis of each of the three contributions to $V^E_m$ 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 $V^E_m$ 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

$$\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2 \tag{12}$$

where $\eta$ is the viscosity of mixture and $\eta_1$ and $\eta_2$ are pure components viscosity. The measured $\eta$ 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 $V^E_m$ for (2-alkanols + acetonitrile) mixtures at 298.15 K.

| System | $\chi_{12}$ (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 |

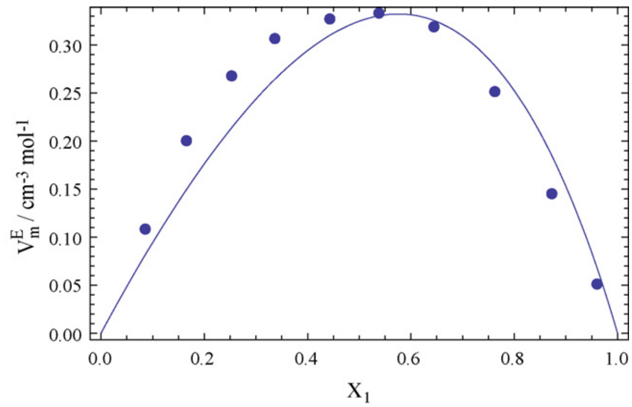


**Fig. 3.** Plot of excess molar volume $V_m^E$ against mole fraction of acetonitrile for the $\{x_1$ acetonitrile + $(1-x_1)$ 2-butanol$\}$ mixtures. (●) Experimental; (– –) calculated by using PFP theory.

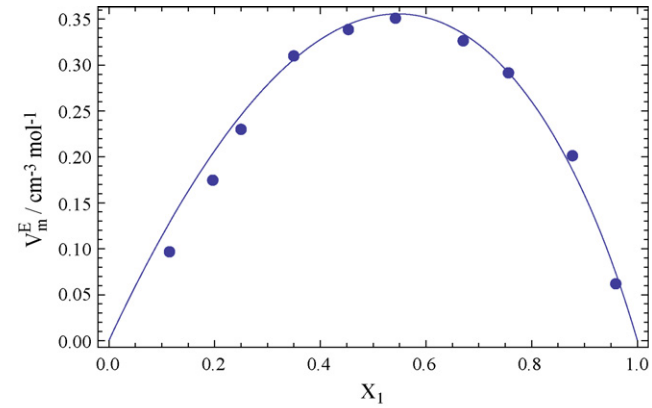


**Fig. 6.** Plot of excess molar volume $V_m^E$ against mole fraction of acetonitrile for the $\{x_1$ acetonitrile + $(1-x_1)$ 2-heptanol$\}$ mixtures. (●) Experimental; (– –) calculated by using PFP theory.

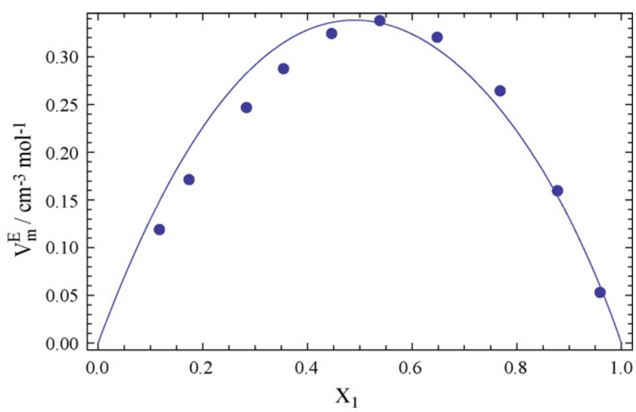


**Fig. 4.** Plot of excess molar volume $V_m^E$ against mole fraction of acetonitrile for the $\{x_1$ acetonitrile + $(1-x)$ 2-pentanol$\}$ mixtures. (●) Experimental; (– –) calculated by using PFP theory.

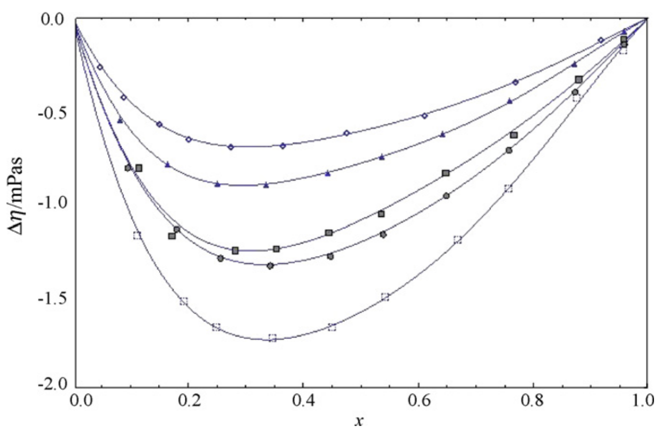


**Fig. 7.** Viscosity deviations of binary mixtures for acetonitrile with (◊) 2-propanol, (▲) 2-butanol, (■) 2-pentanol, (●) 2-hexanol, (□) 2-heptanol at 298.15 K.

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.

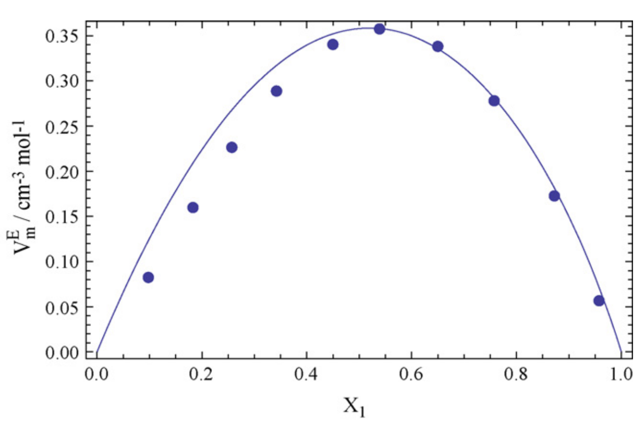


**Fig. 5.** Plot of excess molar volume $V_m^E$ against mole fraction of acetonitrile for the $\{x_1$ acetonitrile + $(1-x_1)$ 2-hexanol$\}$ mixtures. (●) Experimental; (– –) calculated by using PFP theory.

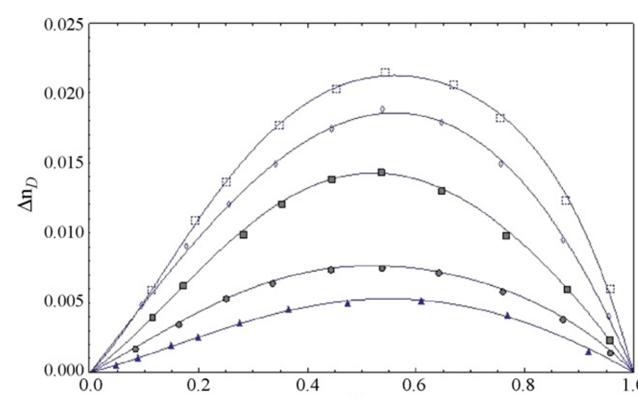


**Fig. 8.** Refractive index deviations on mixing of acetonitrile with (▲) 2-propanol, (●) 2-butanol, (■) 2-pentanol, (◊) 2-hexanol, (□) 2-heptanol at 298.15 K. Solid lines represent the Redlich–Kister fit.

### *3.4. Refractive index*

Refractive index deviations were defined by

$$\Delta n_D = n_D - \{x n^*_{D,1} + (1-x) n^*_{D,2}\} \quad (13)$$

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 $\Delta n_D$ 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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