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# Excess parameter studies on binary liquid mixtures of 2-methyl-2-propanol with aliphatic nitriles at different temperatures

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ABSTRACT

Densities (ρ), viscosities (η) and ultrasonic speeds (u) of binary mixtures of 2-methyl-2-propanol (2M2P) with acetonitrile (AN), propionitrile (PN) and butyronitrile (BN) including those of pure liquids were measured over the entire composition range at temperatures 298.15, 303.15 and 308.15 K respectively. The excess molar volume ($V_m^E$) calculated from density data and other volumetric properties, partial molar volumes ($V_{m,1}$ and $V_{m,2}$), and partial molar volumes at infinite dilution of each component have been calculated using two different approaches. Furthermore, other excess thermodynamic properties such as deviations in isentropic compressibility ($\Delta k_s$), ultrasonic speed (Δu) and viscosity (Δη), excess intermolecular free length ($L_f^E$), excess acoustic impedance ($Z^E$) and excess free energy of activation ($\Delta G^{*E}$) are calculated using the experimentally measured ρ, η and u respectively. The variations of these parameters with composition and temperature show the presence of a weak interaction between the participating components in these mixtures.



## 1. Introduction

The ultrasonic studies are extensively used to estimate the thermodynamic properties and predict the intermolecular interactions of binary mixtures [1]. In the chemical industry information on density and viscosity of the liquid mixtures is necessary in different applications for surface facilities, pipeline systems, mass transfer operations etc. [2]. Volumetric properties of binary mixtures in particular, are complex, since they not only depend on solute–solute, solvent–solvent and solute–solvent interactions, but also on the structural effects arising from interstitial accommodation due to the difference in molar volume and free volume between the components present in the solution. Knowledge of several properties including densities and viscosities at different temperatures is required for engineering design and for subsequent operations [3]. Recently, Yongqing et al. [4] and Peng et al. [5] have reported the volumetric properties of binary mixtures to test molecular theories or models of solution in understanding the molecular interactions between components. The present work is the continuation of our earlier studies [1,6] on understanding thermodynamic properties of binary mixtures whose components have relevant industrial applications. Literature survey shows that 2-methyl-2-propanol (2M2P) has been used as one of the components in some binary mixtures [7–11]. However the molecular interactions of 2M2P with aliphatic nitriles based on volumetric, viscometric and acoustic studies have not been reported so far. 2M2P is used in the manufacture of flotation agents, perfumes, paint removers, methacrylate, food flavorings, and also it is used as a denaturant for ethanol, an octane booster in unleaded gasoline, and as a cleaning agent and solvent for pharmaceuticals, waxes and lacquers. Similarly aliphatic liquids belonging to the homologous nitrile series are also used as important industrial solvents. For example, acetonitrile is used in photographic industry, in the extraction and refining of copper and byproduct, ammonium sulfate. Further, acetonitrile is used for dying in textiles and in coating composition. In this paper, we report the density (ρ), viscosity (η) and ultrasonic speed (u) of pure 2M2P, AN, PN and BN and those of their binary mixtures over the entire composition range at 298.15, 303.15 and 308.15 K respectively.

From these experimental data, the values of molar volume ($V_m$), isentropic compressibility ($k_s$), intermolecular free length ($L_f$), acoustic impedance (Z), free energy of activation ($\Delta G^*$), deviations in isentropic compressibility ($\Delta K_s$), ultrasonic speed (Δu) and viscosity (Δη), excess molar volume ($V_m^E$), excess intermolecular free length ($L_f^E$), excess acoustic impedance ($Z^E$) and excess free energy of activation ($\Delta Gc^{*E}$) were calculated. In addition to these, the partial molar volumes, $V_{m,1}$ and $V_{m,2}$ of 2M2P and nitriles in the mixture over the whole composition range and partial volumes, $\overline{V}_1^0$ and $\overline{V}_2^0$ at infinite dilution of each component have been calculated using two different approaches and reported. The variations of these parameters with composition and temperature have been discussed in terms of molecular interaction in these mixtures.

## 2. Experimental methods

AR grade nitriles (E. Merck) and 2M2P (Ranbaxy) were distilled prior to use by standard procedures [12,13] and only the middle

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fractions were used in the experiment. All the chemicals were stored over 0.4 nm molecular sieves to remove water content, if any and degassed just before use. The mixtures were prepared by mass and were kept in special air tight stopper bottles to avoid evaporation. Weight measurement was employed using a single pan electronic balance (AND, Japan HR series 300) with a precision of ±0.1 mg.

Ultrasonic speeds of pure liquids and of their binary mixtures were measured using a single crystal ultrasonic interferometer (F-81, Mittal, New Delhi, India) at an operating frequency of 2 MHz and the reproducibility of velocity was within ±0.03% [1,6]. Densities of the pure liquids and their binary mixtures were measured by using a single capillary pycnometer (Borosil glass) within a reproducibility limit of ±0.0001 g/cm$^3$. The capillary with graduated stem marks has a uniform bore and could be closed by a well fitted glass cap. The marks on the capillary were calibrated with triple distilled water. The pycnometer was kept inside a thermostatic water bath for about 30 min to attain thermal equilibrium condition. The viscosity of the pure liquids and binary mixture was measured by means of a suspended level Ubbelohde viscometer with a flow time of 174 s for distilled water at 303.15 K. As the flow time was greater than 100 s, the kinetic energy corrections are not necessary [14]. The time of flow was measured with an electronic stopwatch capable of recording ±0.01 s. An average of three to four sets of flow times for each mixture was taken for the purpose of calculation of the viscosity. The overall experimental reproducibility was estimated to be $\pm 1.5\times10^{-6}$ mPa s. The Ubbelohde viscometer filled with test liquids and mixtures was allowed to stand for about 30 min in a thermostatic water bath so as to minimize thermal fluctuations. The temperature of the test liquids and their binary mixtures during measurements was maintained to an accuracy of ±0.01 K in an electronically controlled thermostatic water bath.

The experimentally measured density (ρ), viscosity (η) and ultrasonic speed (u) of pure liquids have been compared with literature values in Table 1. The deviations between the experimental and the literature values (expressed in terms of average percentage deviations) for density, ultrasonic speed and viscosity are ±0.11, ±0.44 and ±2.21%, respectively. Similar deviations between the experimental and the literature values (expressed in terms of average percentage deviations) for density, ultrasonic speeds and viscosity have been reported earlier for toluene and homologous nitriles [25] showing the validity of our experimental measurements. Uncertainty values associated with the experimentally measured parameters such as density, ultrasonic speed and viscosity are evaluated based on the "Evaluation of measurement data-Guide to the expression of uncertainty in measurement" JCGM 100:2008 and included with experimental values in the respective tables.

### 2.1. Theory

The thermodynamic parameters like molar volume ($V_m$), isentropic compressibility ($k_s$), intermolecular free length ($L_f$), acoustic impedance (Z), and free energy of activation ($\Delta G^*$) are estimated using the experimentally measured ultrasonic velocity, viscosity and density data of the mixtures using the following standard relations [26–28].

$$V_m = \frac{M_{eff}}{\rho} \tag{1}$$

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

$$L_f = \frac{K}{u\rho^{1/2}} \tag{3}$$

$$Z = u\rho \tag{4}$$

**Table 1**
Experimental density (ρ), viscosity (η) and ultrasonic speed (u) values of pure liquids with literature values.

| Liquids | Density (ρ) (g/cm$^3$) | | Viscosity (η) mPa s | | Velocity (u) (ms$^{-1}$) | |
|---|---|---|---|---|---|---|
| | Exp. | Lit. | Exp. | Lit | Exp. | Lit. |
| *298.15 K* | | | | | | |
| 2M2P | 0.7808 | 0.7809[a] | 4.3898 | 4.3915[b] | 1121.2 | 1123.5[b] |
| AN | 0.7754 | 0.7764[c] | 0.3696 | 0.341[b] | 1271.3 | 1268.5[c] |
| PN | 0.7754 | – | 0.4107 | – | 1252.4 | – |
| BN | 0.7847 | – | 0.5463 | – | 1271.4 | – |
| *303.15 K* | | | | | | |
| 2M2P | 0.7753 | 0.7762[d] 0.775[e] | 3.3792 | 3.379[b] 3.381[b] | 1102.3 | 1104.8[d] |
| AN | 0.7699 | 0.77122[f] | 0.3554 | 0.3501[g] | 1251.9 | 1258.64[f] |
| PN | 0.7669 | 0.77191[f] | 0.3991 | – | 1232.7 | 1237.63[f] |
| BN | 0.7803 | 0.78172[f] | 0.5255 | – | 1252.2 | 1260[h] |
| *308.15 K* | | | | | | |
| 2M2P | 0.7701 | – | 2.6427 | 2.6448[b] | 1082.8 | – |
| AN | 0.7647 | 0.7662[i] | 0.3414 | 0.3285[j] | 1231.7 | 1239[k] |
| PN | 0.7652 | 0.7646[l] | 0.3822 | – | 1213.7 | – |
| BN | 0.7759 | – | 0.5049 | – | 1233.9 | – |

[a] Ref. [15].
[b] Ref. [8].
[c] Ref. [16].
[d] Ref. [10].
[e] Ref. [17].
[f] Ref. [18].
[g] Ref. [19].
[h] Ref. [20].
[i] Ref. [21].
[j] Ref. [22].
[k] Ref. [23].
[l] Ref. [24].

$$\Delta G^* = RT\ ln\left[\frac{\eta V}{hN}\right] \tag{5}$$

where $M_{eff}$ is the effective molecular weight [$M_{eff}=(x_1M_1+x_2M_2)$], where $M_1$, $M_2$, $x_1$ and $x_2$ are the molecular weights and the mole fractions of 2M2P and nitriles respectively. K is the Jacobson's constant [29] that depends on temperature and is given by [$K=(93.875+0.375\,T)\times10^{-8}$], R is the universal gas constant, and T being the absolute temperature. h and N are the Planck's constant and the Avogadro number respectively.

Thermodynamic excess functions are found to be very sensitive toward mutual interactions between the component molecules of the binary mixtures. The sign and the extent of deviation of the functions from ideality depend on the strength of interactions between unlike molecules [30,31]. The deviations in isentropic compressibility ($\Delta k_s$) ultrasonic speed (Δu) and viscosity (Δη), excess molar volume ($V_m^E$), excess intermolecular free length ($L_f^E$), excess acoustic impedance ($Z^E$) and excess free energy of activation ($\Delta G^{*E}$) are calculated using the general relation

$$Y^E = Y-[x_1Y_1 + x_2Y_2] \tag{6}$$

where Y represents $V_m/k_s/L_f/u/Z/\eta$ or $\Delta G^*$of the mixture. x is the mole fraction, and subscripts 1 and 2 refer to solvent and solute respectively.

The excess functions $\Delta k_s$, Δu, Δη, $V_m^E$, $L_f^E$, $Z^E$ and $\Delta G^{*E}$ are fitted to a Redlich–Kister type [32] of polynomial equation,

$$Y^E = x(1-x)\sum_{i=1}^{5} A_i(1-2x)^{i-1} \tag{7}$$

where $Y^E$ is $V_m^E/\Delta k_s/\Delta u/L_f^E/Z^E/\Delta\eta$ or $\Delta G^{*E}$. The values of $A_i$ are evaluated by using least squares method with all points weighed