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## Notes

# Molecular interaction in binary mixtures of 1,4-butanediol+picolines: Viscometric approach

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The viscosity (η) of {1,4-butanediol (i) + α-, or β-, or γ-picoline (j)}binary mixtures have been measured and reported at 303.15, 308.15, 313.15 and 318.15 K over the entire range of composition. Viscosity deviation ($\Delta\eta$) and excess Gibbs energy of activation of viscous flow ($\Delta G^{*E}$) based on Eyring's theory have been evaluated and the results fitted to the Redlich-Kister equation. The Δη values are observed to be negative over the entire range of composition for (1,4-butanediol+α-picoline), (1,4-butanediol+β-picoline) and (1,4-butanediol+γ-picoline) systems. The experimental viscosity data have been compared with some well-known equations of Frenkel, modified Frenkel approach and predictive ones like McAllister, Grunberg-Nissan, Hind *et al*., Tamura Kurata and Katti-Chaudhri. The effects of molecular sizes and shapes of the component molecules on the molecular interactions present thereof in the mixtures have been discussed.

**Keywords:** Solution chemistry, Thermodynamic properties, Transport properties, Viscosity, 1,4-butanediol, Picoline, Excess gibbs energy of activation, Molecular interaction, Deviation in viscosity

Viscometric properties of binary and multicomponent liquid mixtures are very useful in understanding the nature and physico-chemical behavior of molecular systems[1-4]. For process design in petroleum, petrochemical, chemical and other related industries involving fluid transportation, mixing, agitation, filtration, heat exchange and concentration, viscosity plays an important role. The estimation of viscosity mixture is more difficult than that of a pure compound. The prediction of viscosity of a liquid mixture is a long standing goal of both experimental and theoretical importance. The experimental data of viscosity at any given temperature and composition for binary mixtures is needed for many industrial, chemical processes or laboratory works[5,6]. In the present investigation, transport and thermodynamic properties of binary mixtures of 1,4-butanediol with picolines are reported at varying temperatures.

1,4-Butanediol is a clear viscous liquid, which is miscible with water and most polar organic solvents. The presence of two hydroxyl groups in vicinal positions (at positions 1 and 4) of this diol makes it suitable as a useful chemical intermediate in the manufacture of many chemical products[7-15]. Picoline refers to three different methylpyridine isomers, all three of which are colourless liquids at room temperature and pressure and are miscible with water and most organic solvents. The picolines are cyclic compounds with molecules having nitrogen atom in the aromatic ring. The nitrogen atom has one lone pair of electrons and is capable of forming the hydrogen bond with a proton-donating molecule. α-Picoline is used as an adhesive for textile tire cord and also a precursor to the agrochemical, nitrapyrin, which prevents loss of ammonia from fertilizers. β-Picoline is a useful precursor to agrochemicals, such as chlorpyrifos and used to make antidotes for poisoning by organophosphate acetylcholinesterase inhibitors.

The binary systems of 1,4-butanediol with α-picoline, β-picoline and γ-picoline are of considerable interest for investigating the intra- and inter-molecular behavior of solvent systems. To the best of our knowledge, no work has been carried on these systems from the point of view of their viscometer behavior. This fact allows us to plan some extensive studies in this field to investigate the interactions between the unlike molecules by examining the transport and thermodynamic parameters. In the present investigation, we have reported the viscosity ($\eta$) of binary mixtures of 1,4-butanediol with picolines at 303.15, 308.15, 313.15 and 318.15 K over the entire composition range. From the experimental values of viscosity, the deviations in viscosity ($\Delta\eta$) have been calculated. The Absolute Average Percentage Deviation (AAPD) has been employed as a tool to get a measure of how far the theoretical approach deviates from the experimental. Furthermore, excess Gibbs energy of activation of viscous flow ($\Delta G^{*E}$) have also been evaluated. The results are fitted to the Redlich-Kister polynomial equation.

## Experimental

1,4-Butanediol (Chemlab, mass fraction purity 0.99) and picolines (Chemlab, GC mass fraction purity 0.99) used in this study were purified by standard methods[16,17]. Before use, the chemicals were stored over 0.4 nm molecular sieves for 72 to remove water content, if any, and were degassed at low pressure. The mixtures were prepared by mass and were kept in special airtight stoppered glass bottles to avoid evaporation. The weighings were done with an electronic balance (CPA-225D, Sartorius, Germany) with a precision of ± 0.1 mg.

The viscosities of pure liquids and their binary mixtures were measured by means of an Ostwald's viscometer. The viscometer was calibrated with triply distilled water at $T$ = (303.15, 308.15, 313.15 and 318.15) K. The viscometer containing the sample to be tested was allowed to stand for around 30 min in a thermostatic water bath so as to minimize any possible thermal fluctuations in the viscometer. The time of flow was recorded in triplicate with a digital stop-watch with an accuracy of ±0.01 s. The temperature of the test liquids during the measurements was maintained to an accuracy of ±0.02 K in an electronically controlled thermostatic water bath. The viscosity η was calculated from the following relationship[18]:

$$\frac{\eta}{\eta_w} = \frac{\rho\, t}{\rho_w\, t_w}$$

where $\eta$, $\rho$, $t$ and $\eta_w$, $\rho_w$, $t_w$ are the viscosities, densities and flow time of mixture and water. The values of viscosity and density of pure water were taken from Lange's Handbook of Chemistry[19].

The reliability of experimental measurements of viscosity was ascertained by comparing the data of pure liquids with the corresponding values available in the literature[20-23] at the temperatures ranging from 303.15 K to 318.15 K. This comparison is given in Table 1 shows that the experimental and literature values compare well in general.

The experimental viscosities ($\eta$) for 1,4-butanediol with picolines at various temperatures are presented in Table 2.

Table 1 — Viscosity, $\eta$, of the pure components at different temperatures

| Component | $T$ (K) | $\eta$ ($10^{-3}$ N m$^{-2}$ s) | |
|---|---|---|---|
| | | Expt. | Lit.$^{(ref.)}$ |
| 1,4-Butanediol | 303.15 | 55.47 | 55.162$^{(20)}$ |
| | 308.15 | 45.66 | 43.798$^{(20)}$<br>45.24$^{(21)}$<br>44.871$^{22)}$ |
| | 313.15 | 37.53 | 35.250$^{(20)}$ |
| | 318.15 | 30.03 | 28.594$^{(20)}$ |
| α-Picoline | 303.15 | 0.7188 | 0.7121 at 305.15 K$^{(21)}$ |
| | 308.15 | 0.6501 | - |
| | 313.15 | 0.5984 | - |
| | 318.15 | 0.5556 | - |
| β-Picoline | 303.15 | 0.8646 | 0.8661 at 298.15 K$^{(23)}$ |
| | 308.15 | 0.8079 | - |
| | 313.15 | 0.7506 | - |
| | 318.15 | 0.6817 | - |
| γ-Picoline | 303.15 | 0.8359 | 0.8318$^{(22)}$ |
| | 308.15 | 0.7793 | - |
| | 313.15 | 0.7300 | 0.7352$^{(22)}$ |
| | 318.15 | 0.6557 | - |

The viscosity deviation[20] from a linear dependence on mole fraction were calculated from Eq. (1),

$$\Delta\eta = \eta_{mix} - \left(x_1\eta_1 + x_2\eta_2\right) \qquad \ldots(1)$$

where $x$ and $\eta$ are the mole fraction and viscosities, subscripts 1 and 2 represents the 1st and 2nd components respectively. $\eta_{mix}$ is the viscosity of the mixture.

On the basis of the theory of absolute reaction rates[24], the excess Gibbs energy of activation $\Delta G^{*E}$ of viscous flow may be calculated from Eq. (2)

$$\Delta G^{*E} = RT\left[\ln \eta_m V_m - \left(x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2\right)\right] \qquad \ldots(2)$$

where $R$ is the universal gas constant, $T$ the absolute temperature, $V_m$ the molar volume of the mixture and $V_i$ the molar volumes of the pure components of the binary mixture. Molar volumes of α and β-picolines were taken from our earlier paper[7], molar volumes of γ-picoline are given in Table S1 (Supplementary data).

The values of $\Delta\eta$ and $\Delta G^{*E}$ for each mixture have been fitted to Redlich-Kister polynomial equation[25]:

$$\Delta\eta \text{ or } \Delta G^{*E} = x_1(1-x_1)\sum_{i=0}^{m} A_i(2x_1-1)^i \qquad \ldots(3)$$

Apart from expressing $\eta$ as a polynomial fit, several semi-empirical and correlative relations have also been employed to estimate the dynamic viscosity, $\eta$, of

Table 2 — Viscosity ($\eta$) values for the binary mixtures of 1,4-butanediol (1) with picolines (2) at different temperatures

| $x_1$ | $\eta$ ($10^{-3}$ N m$^{-2}$ s) | | | |
|---|---|---|---|---|
| | 303.15 K | 308.15 K | 313.15 K | 318.15 K |
| 1,4-Butanediol+α-picoline | | | | |
| 0.0000 | 0.7188 | 0.6501 | 0.5984 | 0.5556 |
| 0.1236 | 0.9545 | 0.8724 | 0.8120 | 0.7630 |
| 0.2410 | 1.456 | 1.362 | 1.257 | 1.167 |
| 0.3524 | 2.412 | 2.245 | 2.044 | 1.848 |
| 0.4585 | 4.019 | 3.697 | 3.319 | 2.921 |
| 0.5594 | 6.583 | 6.020 | 5.282 | 4.567 |
| 0.6557 | 10.45 | 9.540 | 8.211 | 6.968 |
| 0.7477 | 16.08 | 14.64 | 12.41 | 10.39 |
| 0.8355 | 24.05 | 21.83 | 18.32 | 15.13 |
| 0.9195 | 35.17 | 31.90 | 26.55 | 21.56 |
| 1.0000 | 55.47 | 45.66 | 37.53 | 30.03 |
| 1,4-Butanediol+β-picoline | | | | |
| 0.0000 | 0.8646 | 0.8079 | 0.7506 | 0.6817 |
| 0.1224 | 1.052 | 1.001 | 0.9325 | 0.835 |
| 0.2389 | 1.579 | 1.54 | 1.427 | 1.281 |
| 0.3498 | 2.592 | 2.496 | 2.275 | 2.017 |
| 0.4556 | 4.261 | 4.052 | 3.626 | 3.156 |
| 0.5566 | 6.886 | 6.431 | 5.678 | 4.840 |
| 0.6531 | 10.80 | 9.983 | 8.654 | 7.263 |
| 0.7455 | 16.45 | 15.11 | 12.88 | 10.67 |
| 0.8339 | 24.43 | 22.36 | 18.76 | 15.36 |
| 0.9187 | 35.50 | 32.29 | 26.80 | 21.67 |
| 1.0000 | 55.47 | 45.66 | 37.53 | 30.03 |
| 1,4-Butanediol+γ-picoline | | | | |
| 0.0000 | 0.8359 | 0.7793 | 0.7300 | 0.6557 |
| 0.1224 | 1.218 | 1.137 | 1.051 | 0.926 |
| 0.2389 | 1.963 | 1.826 | 1.666 | 1.450 |
| 0.3498 | 3.148 | 2.913 | 2.614 | 2.248 |
| 0.4556 | 4.965 | 4.564 | 4.032 | 3.431 |
| 0.5566 | 7.671 | 7.022 | 6.113 | 5.141 |
| 0.6531 | 11.60 | 10.59 | 9.100 | 7.560 |
| 0.7455 | 17.19 | 15.65 | 13.29 | 10.93 |
| 0.8339 | 25.02 | 22.73 | 19.09 | 15.54 |
| 0.9187 | 35.81 | 32.47 | 26.97 | 21.77 |
| 1.0000 | 55.47 | 45.66 | 37.53 | 30.03 |

liquid mixtures in terms of pure component data[26,27]. We have examined equations proposed by Frenkel[28], Grunberg-Nissan[29], Tamura-Kurata[30], Katti-Chaudhri[31], McAllister[32] and of Hind *et al.*[33]

Frenkel relation is represented by:

$$\ln \eta = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + 2x_1x_2 \ln \eta_{12} \quad \ldots(4)$$

where $\eta_{12}$ is a constant attributed to unlike pair interactions. Its value is obtained from equation,

$$\eta_{12} = \frac{(\eta_1 + \eta_2)}{2}$$

Dey *et al.*[34] proposed a modified form of interaction parameter, which can be expressed as:

$$\eta_{12} = 2\left(\frac{\eta_1\eta_2}{[\eta_1+\eta_2]}\right) \quad \ldots(4a)$$

The Grunberg-Nissan phenomenological equation reads,

$$\eta = \exp\left(x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1x_2G_{12}\right) \quad \ldots(5)$$

where $G_{12}$ is a parameter proportional to the interchange energy and has been regarded as an indicator for the nonideal behavior of binary mixtures.

Hind *et al*. relation is expressed as:

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2H_{12} \quad \ldots(6)$$

The Tamura Kurata relation is given as:

$$\eta = x_1\varphi_1\eta_1 + x_2\varphi_2\eta_2 + 2(x_1x_2\varphi_1\varphi_2)^{1/2}T_{12} \quad \ldots(7)$$

Katti and Chaudhri derived the following equation (Eq. 8)

$$\ln \eta V = x_1 \ln V_1\eta_1 + x_2 \ln V_2\eta_2 + x_1x_2K_{12} \quad \ldots(8)$$

All the four of the above correlative equations contain one adjustable parameter. The two-parameter McAllister equation based on the Eyring's theory of absolute reaction rates[24] and three-body interaction model is given by Eq. (9),

$$\begin{aligned}\ln \eta = {} & x_1^3 ln\eta_1 + 3x_1^2x_2 lnZ_{12} + 3x_1x_2^2 lnZ_{21} \\ & + x_2^2 ln\eta_2 - \ln\left(x_1 + x_2\frac{M_2}{M_1}\right) \\ & +3x_1^2x_2 \ln\left(\frac{2}{3} + \frac{M_2}{3M_1}\right) + 3x_1^2x_2 \ln\left(\frac{1}{3} + \frac{2M_2}{3M_1}\right) \\ & + x_2^3 \ln\left(\frac{M_2}{M_1}\right) \quad \ldots(9)\end{aligned}$$

where $Z_{12}$ and $Z_{21}$ are interaction parameters and $M_i$ and $\eta_i$ are the molecular mass and kinematic viscosity of pure component i.

Absolute Average Percentage Deviation (AAPD) has been employed as a tool[33,36] to obtain a measure of how far the theoretical approach deviates from the experimental for a system. It is given by the following relation:

$$\text{AAPD} = \frac{1}{n}\sum\left|\frac{\eta_{\text{expt}} - \eta_{\text{theoret}}}{\eta_{\text{expt}}}\right| \times 100 \quad \ldots(10)$$

## Results and discussion

A comparison of experimentally determined values of viscosity, $\eta$, measured for all pure liquids at 303.15 K, 308.15 K, 313.15 K and 318.15 K, with literature values are presented in Table 1. Experimental values of viscosity, $\eta$, for the three binary mixtures at temperatures of (303.15 K, 308.15 K, 313.15 K and 318.15 K) are presented in Table 2. Table 3 lists

Table 3 — Deviation in viscosity ($\Delta\eta$) and excess Gibbs energy of activation of viscous flow ($\Delta G^{*E}$) of binary mixtures at different temperatures

| $x_1$ | $\Delta\eta$ ($10^{-3}$ N m$^{-2}$ s) | | | | $\Delta G^{*E}$ ( kJ mol$^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|
| | 303.15 K | 308.15 K | 313.15 K | 318.15 K | 303.15 K | 308.15 K | 313.15 K | 318.15 K |
| 1,4-Butanediol+α-picoline | | | | | | | | |
| 0.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1236 | -6.534 | -5.343 | -4.354 | -3.438 | -0.2152 | -0.2162 | -0.2019 | -0.1836 |
| 0.2410 | -12.46 | -10.13 | -8.242 | -6.492 | -0.2856 | -0.2676 | -0.2525 | -0.2317 |
| 0.3524 | -17.60 | -14.27 | -11.57 | -9.096 | -0.2594 | -0.2471 | -0.2335 | -0.2221 |
| 0.4585 | -21.80 | -17.59 | -14.21 | -11.15 | -0.2058 | -0.2034 | -0.1915 | -0.1910 |
| 0.5594 | -24.77 | -19.80 | -15.98 | -12.48 | -0.1473 | -0.1485 | -0.1463 | -0.1469 |
| 0.6557 | -26.17 | -20.62 | -16.61 | -12.92 | -0.0989 | -0.1004 | -0.1044 | -0.1077 |
| 0.7477 | -25.57 | -19.66 | -15.80 | -12.21 | -0.0617 | -0.0647 | -0.0714 | -0.0742 |
| 0.8355 | -22.41 | -16.42 | -13.14 | -10.06 | -0.0344 | -0.0392 | -0.0460 | -0.0468 |
| 0.9195 | -15.89 | -10.14 | -8.016 | -6.111 | -0.0145 | -0.0185 | -0.0210 | -0.0242 |
| 1.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 1,4-Butanediol+β-picoline | | | | | | | | |
| 0.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1224 | -6.496 | -5.296 | -4.320 | -3.439 | -0.1942 | -0.1774 | -0.1590 | -0.1521 |
| 0.2389 | -12.33 | -9.980 | -8.110 | -6.412 | -0.2719 | -0.2275 | -0.2027 | -0.1820 |
| 0.3498 | -17.37 | -14.00 | -11.34 | -8.931 | -0.2430 | -0.2069 | -0.1853 | -0.1640 |
| 0.4556 | -21.48 | -17.19 | -13.88 | -10.90 | -0.1920 | -0.1639 | -0.1480 | -0.1323 |
| 0.5566 | -24.37 | -19.34 | -15.55 | -12.18 | -0.1377 | -0.1231 | -0.1083 | -0.1013 |
| 0.6531 | -25.73 | -20.12 | -16.12 | -12.59 | -0.0929 | -0.0852 | -0.0765 | -0.0733 |
| 0.7455 | -25.12 | -19.14 | -15.29 | -11.89 | -0.0588 | -0.0542 | -0.0505 | -0.0485 |
| 0.8339 | -21.97 | -15.85 | -12.67 | -9.795 | -0.0326 | -0.0287 | -0.0298 | -0.0287 |
| 0.9187 | -15.53 | -9.722 | -7.739 | -5.973 | -0.0117 | -0.0110 | -0.0124 | -0.0136 |
| 1.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 1,4-Butanediol+γ-picoline | | | | | | | | |
| 0.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1224 | -6.305 | -5.135 | -4.184 | -3.326 | -0.0337 | -0.0394 | -0.0392 | -0.0494 |
| 0.2389 | -11.92 | -9.672 | -7.855 | -6.222 | -0.0324 | -0.0440 | -0.0491 | -0.0626 |
| 0.3498 | -16.80 | -13.56 | -10.99 | -8.684 | -0.0168 | -0.0332 | -0.0434 | -0.0613 |
| 0.4556 | -20.76 | -16.66 | -13.47 | -10.61 | -0.0015 | -0.0223 | -0.0365 | -0.0546 |
| 0.5566 | -23.57 | -18.74 | -15.10 | -11.87 | 0.0100 | -0.0117 | -0.0281 | -0.0454 |
| 0.6531 | -24.92 | -19.50 | -15.67 | -12.28 | 0.0147 | -0.0034 | -0.0197 | -0.0376 |
| 0.7455 | -24.37 | -18.58 | -14.88 | -11.63 | 0.0177 | 0.0021 | -0.0130 | -0.0304 |
| 0.8339 | -21.38 | -15.47 | -12.33 | -9.611 | 0.0147 | 0.0020 | -0.0073 | -0.0222 |
| 0.9187 | -15.22 | -9.536 | -7.570 | -5.879 | 0.0098 | 0.0012 | -0.0049 | -0.0132 |
| 1.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

deviation in viscosity, $\Delta\eta$, and excess Gibbs free energy of activation of viscous flow, $\Delta G^{*E}$, for the three binary mixtures at four different temperatures as a function of mole fraction of 1,4-butanediol. The coefficients $A_i$ of Eq. (3) and the standard deviations $\sigma$ for $\Delta\eta$ and $\Delta G^{*E}$ for the three mixtures at four different temperatures are given in Table 4.

The experimental results for $\Delta\eta$ and $\Delta G^{*E}$ for the three binary mixtures against mole fraction of 1,4-butanediol at temperature 303.15 K are plotted in Figs 1 and 2. The deviations in viscosity (Fig. 1) for all the three mixtures were found to be negative over the entire concentration range of the mixtures with a maximum negative value at $x_1$ = 0.65, and negative $\Delta\eta$ values decreases with increasing temperature for all mixtures. An increase in temperature decreases the self-association of pure components and heteroassociation between unlike molecules, because

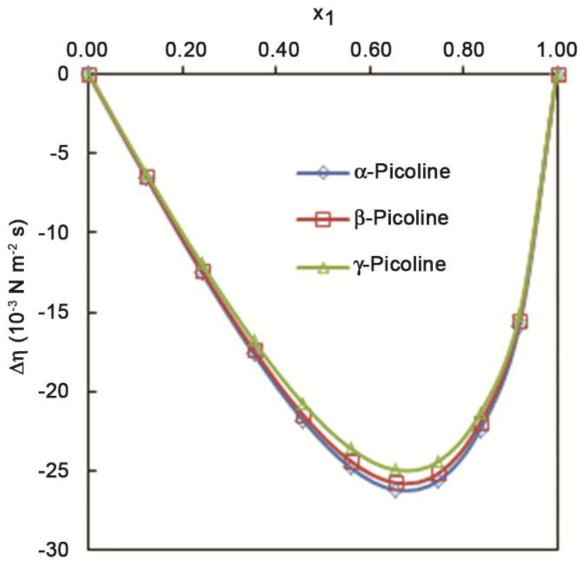

Fig. 1 — Plots of deviation in viscosity ($\Delta\eta$) versus mole fraction of 1,4-butanediol ($x_1$) of binary mixtures of 1,4-butanediol (1) with picolines (2) [α-picoline (◊); β-picoline (□); γ-picoline (Δ)] at 303.15 K.

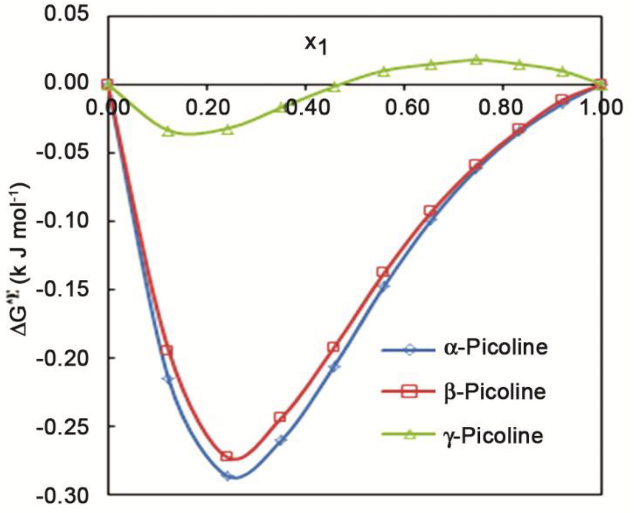

Fig. 2 — Plots of excess Gibbs energy of activation of viscous flow ($\Delta G^{*E}$) versus mole fraction of 1,4-butanediol ($x_1$) of binary mixtures of 1,4-butanediol (1) with picolines (2) [α-picoline (◊); β-picoline (□); γ-picoline (Δ)] at 303.15 K.

Table 4 — Coefficients ($A_i$) and standard deviations ($\sigma$) of Eq. (3)

| Property | Temp. (K) | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | σ |
|---|---|---|---|---|---|---|---|
| | 1,4- butanediol+α-picoline | | | | | | |
| $\Delta\eta$ ($10^{-3}$ N m$^{-2}$ s) | 303.15 | -93.194 | -57.310 | -20.327 | -44.223 | -58.093 | 0.258 |
| | 308.15 | -74.511 | -46.177 | -21.728 | -10.188 | -5.044 | 0.009 |
| | 313.15 | -60.164 | -36.842 | -18.239 | -6.934 | -1.085 | 0.015 |
| | 318.15 | -47.128 | -28.025 | -12.726 | -4.279 | -0.952 | 0.003 |
| $\Delta G^{*E}$ (kJ mol$^{-1}$) | 303.15 | -0.723 | 1.190 | -0.875 | -0.018 | 0.342 | 0.002 |
| | 308.15 | -0.721 | 1.040 | -0.597 | 0.185 | -0.218 | 0.001 |
| | 313.15 | -0.690 | 0.915 | -0.686 | 0.209 | -0.024 | 0.001 |
| | 318.15 | -0.692 | 0.812 | -0.435 | 0.164 | -0.227 | 0.001 |
| | 1,4- butanediol+β-picoline | | | | | | |
| $\Delta\eta$ ($10^{-3}$ N m$^{-2}$ s) | 303.15 | -92.100 | -55.400 | -20.100 | -41.800 | -54.700 | 0.245 |
| | 308.15 | -73.100 | -44.200 | -21.100 | -7.190 | -1.960 | 0.008 |
| | 313.15 | -58.900 | -34.500 | -16.400 | -6.030 | -1.800 | 0.006 |
| | 318.15 | -46.200 | -26.400 | -12.100 | -3.870 | -1.710 | 0.002 |
| $\Delta G^{*E}$ (kJ mol$^{-1}$) | 303.15 | -0.666 | 1.140 | -0.992 | -0.103 | 0.675 | 0.003 |
| | 308.15 | -0.583 | 0.875 | -0.697 | 0.188 | 0.196 | 0.001 |
| | 313.15 | -0.521 | 0.785 | -0.649 | 0.122 | 0.167 | 0.0004 |
| | 318.15 | -0.475 | 0.634 | -0.513 | 0.313 | -0.114 | 0.0005 |
| | 1,4- butanediol+γ-picoline | | | | | | |
| $\Delta\eta$ ($10^{-3}$ N m$^{-2}$ s) | 303.15 | -89.100 | -53.600 | -19.400 | -42.100 | -55.900 | 0.250 |
| | 308.15 | -70.800 | -42.700 | -20.500 | -8.400 | -3.620 | 0.003 |
| | 313.15 | -57.200 | -33.700 | -15.800 | -6.080 | -2.590 | 0.004 |
| | 318.15 | -45.000 | -26.000 | -12.100 | -4.440 | -1.870 | 0.002 |
| $\Delta G^{*E}$ (kJ mol$^{-1}$) | 303.15 | 0.016 | 0.229 | -0.225 | 0.103 | 0.044 | 0.001 |
| | 308.15 | -0.069 | 0.218 | -0.143 | 0.068 | -0.079 | 0.001 |
| | 313.15 | -0.069 | 0.218 | -0.143 | 0.068 | -0.079 | 0.001 |
| | 318.15 | -0.202 | 0.167 | -0.169 | 0.045 | -0.045 | 0.0003 |

Table 5 — The AAPD values calculated from Eq. (10)

| System | *T* (K) | Frenkel (Eq. 4) | Mod. Frenkel (Eq. 4a) | McAllister (Eq. 9) | Grunberg-Nissan (Eq. 5) | Hind *et al.* (Eq. 6) | Tamura-Kurata (Eq. 7) | Katti-Chaudhri (Eq. 8) |
|---|---|---|---|---|---|---|---|---|
| 1,4-butanediol+ α-picoline | 303.15 | 105.04 | 29.48 | 1.98 | 7.06 | 95.82 | 88.24 | 7.39 |
| | 308.15 | 101.93 | 30.46 | 1.84 | 6.46 | 93.97 | 85.71 | 6.80 |
| | 313.15 | 94.35 | 30.23 | 1.67 | 5.61 | 81.37 | 73.93 | 5.97 |
| | 318.15 | 85.90 | 29.63 | 1.20 | 4.86 | 67.41 | 60.95 | 5.23 |
| 1,4-butanediol+ β-picoline | 303.15 | 98.06 | 29.66 | 1.84 | 6.61 | 85.23 | 78.62 | 6.91 |
| | 308.15 | 91.91 | 31.09 | 1.50 | 5.41 | 79.30 | 72.95 | 5.72 |
| | 313.15 | 84.42 | 30.94 | 1.37 | 4.70 | 68.06 | 62.36 | 5.03 |
| | 318.15 | 77.90 | 30.53 | 1.30 | 4.09 | 58.74 | 53.65 | 4.48 |
| 1,4-butanediol+ γ-picoline | 303.15 | 75.79 | 37.21 | 1.76 | 5.20 | 77.13 | 66.93 | 5.62 |
| | 308.15 | 74.39 | 37.18 | 1.29 | 4.90 | 62.41 | 68.28 | 4.87 |
| | 313.15 | 69.79 | 36.08 | 1.13 | 3.66 | 51.35 | 59.31 | 4.93 |
| | 318.15 | 66.12 | 35.09 | 1.58 | 3.99 | 44.54 | 45.02 | 4.02 |

of the increase of thermal energy. This leads to less negative values of $\Delta\eta$ with increasing temperature as observed in the present study. Similar temperature dependence has been reported by Marigliano[33]. Curves are found skewed towards the 1,4-butanediol rich region. The cohesive forces between the pairs of unlike molecules are far less than the forces between the pairs of like molecules. As a result, negative deviations in the viscosity are observed. In general for the systems, where dispersion and dipolar interactions are operating, $\Delta\eta$ values are found to be negative, whereas charge transfer, hydrogen bonding interactions and other chemical forces leading to the formation of complex species between unlike molecules result in positive values of $\Delta\eta$. The actual values would be dependent upon the dominant factor. The negative values of the deviation in viscosity suggest the existence of weak intermolecular interactions upon mixing.

A look at Table 2 reveals that all the binary mixtures under consideration show similar trends with variation in temperature. Beyond the equimolar region, 1,4-butanediol being the more viscous liquid becomes dominant with a quick jump in the mixture viscosity values.

Table 3 and Fig. 2 show that the excess Gibbs energy of activation of viscous flow ($\Delta G^{*E}$) for the 1,4-butanediol and γ-picoline at 303.15 K and 308.15 K are positive over a certain range of mole fraction. This trend is quite different from the other two systems where all the values are seen to be negative over the entire range of mole fraction over the temperature range. These results suggest that the intermolecular interactions are more prevalent in the γ-picoline system at these two temperatures as compared to the other isomers. On the whole the excess values are less in magnitude as compared to its α- and β-counterparts. This observation seen in the present investigation is complemented by literature survey[35] which shows that the reactivity of isomeric picolines during oxidative ammonolysis on a vanadium oxide catalyst is highest for the γ-picoline. This may be resulting from dominance of structural effects over effects arising from interactions occurring due to mixing[36]. Previously reported values[37-39] of excess Gibbs free energy of activation of viscous flow ($\Delta G^{*E}$) indicate that the positive values point towards stronger and specific interactions and vice versa.

Literature survey reveals that amongst the various equations employed for prediction of viscosity, the Frenkel relation gives reasonably good agreement on comparing with experimental findings[40,41]. The Frenkel approach is different from the majority of the predictive approaches due to the presence of an interaction parameter ($\eta_{12}$) which represents an average of the viscosity values of pure components. Dey *et al.*[34] have recently proposed a modified Frenkel approach and tested the proposed model on a number of binary and higher order liquid mixtures. In the present investigation, the modified Frenkel model has been compared with the viscosity values evaluated by the original Frenkel approach.

The results (Table 5) clearly indicate the improved predictive capability of the modified Frenkel approach[34] as compared to the original one. In almost all the system over the entire range of temperature, the modified approach is seen to better the original Frenkel approach by 100% or more. The Frenkel approach does not give a very satisfactory performance due to the vast difference in the viscosity values of the components comprising the binary mixture. The modified Frenkel interaction parameter thus exhibits much improved predictive capability as compared to its original counterpart.

As expected, the McAllister correlative model is able to predict viscosity with a much high degree of precision as compared to the rest of the correlative approaches taken for comparison. It is pertinent to note that for all the systems under consideration over the entire range of the temperature, the modified Frenkel approach performs better than both Hind and the Tamura Kurata approach which are correlative in nature. The lowest AAPD values are seen for the 1,4-butanediol + γ-picoline system (Table 5) for all the approaches taken for comparison and the highest values are recorded for the 1,4-butanediol + α-picoline system.

In summary deviations in viscosity and excess Gibbs free energy of activation of viscous flow for three systems comprising of 1,4-butanediol +α-picoline, 1,4-butanediol+β-picoline and 1,4-butanediol +γ-picoline in the temperature range of $T$= 303.15 K to 318.15 K have been reported. The deviations in viscosity are negative for all the systems under consideration. The observed values of $\Delta\eta$ and $\Delta G^{*E}$ suggest the existence of specific interactions between unlike molecules with the highest interactions being exhibited by the 1,4-butanediol+γ-picoline system as compared to its α- and β-counterpart systems. A comparative study has been carried out using various predictive and correlative approaches for predicting viscosity using AAPD as the criterion for predictive capability. A recently developed viscosity model shows promising predictive capability as compared to some well-known approaches.

## Supplementary data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_56A(11)1154-1160_SupplData.pdf.

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