Molar Interactions of Some Aromatic Hydrocarbons in \( n \)-Heptane by Viscometric Measurements at 298.15 K

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Abstract

The viscosities, \( \eta \), of pure \( n \)-heptane, toluene, \( o \)-xylene, mesitylene, and some of their binary mixtures covering the whole composition range have been measured at 298.15 K. Deviations in viscosity, \( \Delta \eta \), was calculated using experimental results. The concentration dependencies of \( \eta \) were correlated to polynomial expressions, whereas, \( \Delta \eta \) were fitted to the Redlich–Kister equation. Moreover, the values of the excess Gibbs free energy of activation, \( \Delta G^{\#E} \), of these mixtures were determined. Viscosity measurements of the binary systems were correlated with Grunberg and Nissan the three-body and four-body McAllister expressions. In all systems, \( \Delta \eta \) were found to be negative in the whole range of composition with a single lobe having minimum at 0.6 mple fraction of aromatic hydrocarbon. While dispersive forces are suggested to dominate in \( n \)-heptane + toluene, for the other two systems ‘favourable geometric fitting’ overpowers them due to the increasing number of – CH\(_3\) groups in the relevant aromatic hydrocarbons.

Keywords: Viscosity; \( n \)-heptane; Aromatic hydrocarbon.
1. Introduction

As a transport property the applications of viscosity are vast, including those used in many chemical and industrial processes, such as, design of new processes and process equipments. So, calculation of viscosity from theoretical point of view is also highly desirable. There has been a recent upsurge of interest in the study of properties of binary liquid mixtures [1-5]. The present report is a part of our ongoing studies on molecular interactions in binary liquid systems focusing particularly on those of aromatic and aliphatic hydrocarbons [3,4]. After dealing
with density related properties of n-heptane + aromatic hydrocarbons [4] here we report on their viscometric properties at 298.15 K.

Aliphatic hydrocarbons are basically known as non-polar and acting forces within the molecules are mostly of van der Waals type. In homo and hetero molecular systems of aliphatic hydrocarbons, factors that influence the strength of interaction are: i) chain length, ii) branching of carbon chain, iii) size and shape of component molecules, iv) size and shape of the hetero species as a whole etc. Factors that may further influence the strength of interaction having an aromatic hydrocarbon as the second component are supposed also to include nature of aromatic ring, overall size and shape of the aromatic hydrocarbons as well as position and number of groups attached to the aromatic moiety.

Previously, Iloukhani et al [3] studied the volumetric and viscometric properties of toluene + n-alkanes (C\textsubscript{5}-C\textsubscript{10}), while Lal et al. [5] have reported on the same properties of benzene + hexane, + decane, + hexadecane and + squalane. However, Aminabhavi and Patil [6] measured the densities, refractive indices and viscosities for ethylbenzene + n-alkanes (C\textsubscript{6}-C\textsubscript{11}) between 298.15 and 308.15 K. The present investigation therefore reports on the viscosity and the interaction for the systems of n-heptane (NHP) + toluene (TN), + o-xylene (OXN) and + mesitylene (MSN) in the entire range of composition at 298.15 K. Keeping the aliphatic hydrocarbon fixed, here the number of substitutes is varied in the aromatic hydrocarbons. This would further enable us to find the effect due to increment in the number of substituent as well as variation in its position in the aromatic hydrocarbons. So far, such data on the system of (NHP+ MSN) is yet to be reported.
2. Experimental Section

The liquids (NHP), (OXN), (MSN) were obtained Aldrich with a mass fraction purity of >99% and (TN) (Merck, >99% mass fraction purity) were used without further purification except that being kept over molecular sieves (4A°) for 2-3 weeks. Binary mixtures of various compositions were prepared by mass, mixing pure components at different proportions with the help of an electronic balance (College B 204-S, Mettler Toledo) accurate up to ±0.0001 g. The Ostwald Viscometer (Technico, PSL BS/U, A-type) was used to measure the viscosity $\eta$. The flow time of liquids was recorded by an electronic stopwatch reading up to ±0.1 s. For all measurements, a thermostated water bath controlled up to ±0.01 K was used. The mole fraction was accurate up to ±10$^{-4}$, while the uncertainty in measured $\eta$ was estimated as ±2×10$^{-3}$ mPa.s. The purity of the liquids was ascertained by further comparing their viscosities with the corresponding literature values at 298.15 K as tabulated in Table 1.

Table 1. Comparison of experimental viscosities, $\eta$ of pure liquids at 298.15 K.

| Sample | $\eta$/mPa.s |
|--------|--------------|
| This work | Literature |
| (NHP) | 0.3865 | 0.395[3] |
| (TN) | 0.5555 | 0.5531[7] |
| (OXN) | 0.7510 | 0.755[8] |
| (MSN) | 0.6486 | 0.656[9] |
3. Results and Discussion

3.1. Viscosities

Experimental values of viscosities, $\eta$, of mixtures NHP + TN, NHP + OXN and NHP + MSN at 298.15 K are listed as a function of mole fraction in Table 2. At a particular temperature, $\eta$ values were fitted to a four-degree polynomial equation of the form:

$$\eta / \text{mPa} \cdot \text{S} = \sum_{i=0}^{n} a_i x_2^i$$

(1)

The average absolute deviation (AAD%) was calculated by following the equation [10]:

$$AAD\% = \frac{1}{N_p} \sum_{i=1}^{N_p} \left[ \frac{\eta_i^{\text{exp}} - \eta_i^{\text{cal}}}{\eta_i^{\text{exp}}} \right] \times 100$$

(2)

where, $N_p$ is the number of experimental points, and $\eta_i^{\text{exp}}$ and $\eta_i^{\text{cal}}$ are the experimental and calculated viscosities of the $i$-th mixture. The values AAD% are tabulated in Table 3. Fig. 1 indicates the comparative diagram of $\eta$ against $x_2$ of the three systems at 298.15 K. The $\eta$ of pure liquids varies in the order: OXN > MSN > TN > NHP. For their binary mixtures, $\eta$ increases systematically as the concentration of the aromatic hydrocarbon $x_2$ increases and the order of increment follow is found to in viscosity: NHP + OXN > + MSN > + TN.
3.2 Deviations in Viscosity

From experimental $\eta$, the viscosity deviations $\Delta\eta$ were calculated using equations as in [11, 12]:

$$\Delta\eta = \eta - \eta_1 x_1 - \eta_2 x_2$$  \hspace{1cm} (3)

where, $\eta$ is the viscosity of solution, $\eta_1$ and $\eta_2$ are viscosities and $x_1$ and $x_2$ are the mole fractions of pure components 1 and 2, respectively. The estimated values of $\Delta\eta$ were correlated well by the Redlich-Kister equation [13]:

$$\Delta\eta = x_2 (1 - x_2) \sum_{i=0}^{n} A_i (2x_2 - 1)^i$$  \hspace{1cm} (4)

where, $A_i$ is the fitting coefficient and $x_2$ is the mole fraction of the aromatic hydrocarbons.

The standard deviation, $\sigma$, followed the equation:

$$\sigma = \left[ \frac{\sum (\Delta\eta_{obs} - \Delta\eta_{cal})^2}{n - p - 2} \right]^{1/2}$$  \hspace{1cm} (5)

where, $\Delta\eta_{obs}$ and $\Delta\eta_{cal}$ are the observed and calculated deviations in viscosity, $n$ is the total number of compositions and $p$ is the number of coefficients. The
coefficients $A_i$ and $\sigma$ are as shown in Table 3. Fig. 2 depicts the variation of $\Delta\eta$ with the mole fraction $x_2$. The deviation in viscosity, $\Delta\eta$ values of many organic liquids with aromatic hydrocarbons are characterized by negative and very low values [14–18]. In the present systems, $\Delta\eta$ were negative in the whole range of composition forming a single lobe with minima at $x_2$~0.6. At a particular temperature, $\Delta\eta$ variation followed the order: NHP + OXN > NHP > TN > + MSN.

**Table 2.** Viscosities, $\eta$ (mPa.s), and deviations in viscosity, $\Delta\eta$ (mPa.s), of the systems of NHP ($x_1$) + TN ($x_2$), + OXN ($x_2$) and + MSN ($x_2$) for different molar ratios at 298.15 K.

| $x_2$ | $\eta$ | $\Delta\eta$ | $x_2$ | $\eta$ | $\Delta\eta$ | $x_2$ | $\eta$ | $\Delta\eta$ |
|-------|--------|---------------|-------|--------|---------------|-------|--------|---------------|
| NHP ($x_1$) + TN ($x_2$) | NHP ($x_1$) + OXN ($x_2$) | NHP ($x_1$) + MSN ($x_2$) |
| 0.0000 | 0.3865 | 0.0000 | 0.0000 | 0.3865 | 0.0000 | 0.0000 | 0.3865 | 0.0000 |
| 0.1001 | 0.3902 | -0.0132 | 0.1001 | 0.4008 | -0.0222 | 0.1000 | 0.4009 | -0.0118 |
| 0.1991 | 0.3953 | -0.0248 | 0.2000 | 0.4183 | -0.0411 | 0.1993 | 0.4167 | -0.0220 |
| 0.3002 | 0.4014 | -0.0358 | 0.3005 | 0.4396 | -0.0564 | 0.3000 | 0.4353 | -0.0299 |
| 0.3996 | 0.4102 | -0.0438 | 0.3999 | 0.4635 | -0.0688 | 0.4000 | 0.4563 | -0.0351 |
| 0.5000 | 0.4221 | -0.0489 | 0.5000 | 0.4915 | -0.0773 | 0.5000 | 0.4798 | -0.0378 |
| 0.6000 | 0.4369 | -0.0510 | 0.6002 | 0.5255 | -0.0798 | 0.5998 | 0.5053 | -0.0384 |
| 0.6999 | 0.4557 | -0.0491 | 0.7001 | 0.5645 | -0.0772 | 0.6992 | 0.5345 | -0.0353 |
| 0.8001 | 0.4786 | -0.0431 | 0.8001 | 0.6130 | -0.0651 | 0.7990 | 0.5687 | -0.0273 |
| 0.9001 | 0.5093 | -0.0293 | 0.9000 | 0.6706 | -0.0439 | 0.9000 | 0.6053 | -0.0171 |
| 1.0000 | 0.5555 | 0.0000 | 1.0000 | 0.7510 | 0.0000 | 1.0000 | 0.6486 | 0.0000 |
Table 3. Coefficients, $a_i$, of polynomial equation (1) for viscosity, $\eta$ (mPa.s) and AAD% and fitting coefficients, $A_i$ and standard deviation, $\sigma$ for deviations in viscosity, $\Delta \eta$ (mPa.s) for the systems of NHP ($x_1$) + TN ($x_2$), NHP ($x_1$) + OXN ($x_2$) and NHP ($x_1$) + MSN ($x_2$) at 298.15K.

|        | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ | AAD% | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $\sigma$ |
|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|---------|
| NHP ($x_1$) + TN ($x_2$) | 0.387 | 0.006 | 0.207 | -0.266 | 0.220 | 0.5624 | -0.1946 | -0.0701 | -0.0562 | -0.0662 | 0.00048 |
| NHP ($x_1$) + OXN ($x_2$) | 0.386 | 0.103 | 0.329 | -0.390 | 0.326 | 0.7973 | -0.3063 | -0.1114 | -0.0815 | -0.0546 | 0.00086 |
| NHP ($x_1$) + MSN ($x_2$) | 0.386 | 0.130 | 0.110 | -0.018 | 0.039 | 0.4338 | -0.1524 | -0.0294 | -0.0100 | -0.0054 | 0.00048 |

NHP being a simple linear hydrocarbon is non-polar and characterized by quite low density, while the alkylated aromatic hydrocarbons (TN, OXN and MSN) are weakly polar due to the presence of delocalized $\pi$-electrons below and above the rings. With increasing number of $\text{–CH}_3$ substituents at different positions further enhance their $\pi$-electron density. So that, forces like dipole-dipole, dipole-quadrapole also exist intermolecularly which lead to assume these aromatic hydrocarbons as weakly associated. Therefore, addition of NHP to TN, OXN or MSN comes dispersion initially breaking up the weak forces. As a result viscosity of all the solutions decreases and values of $\Delta \eta$ become negative for all the mixtures with minima $x_2\sim 0.6$ as in Fig. 2.

The above explanation seems to be justified for NHP + TN, because for this particular system $V_m^E$ were observed to be positive due to dominating dispersive forces [4]. But for NHP + OXN and NHP + MSN, the $\Delta \eta$ are negative in spite of negative $V_m^E$. In the latter systems, all the species within the mixtures get closer
together forming close-packed structures possibly due to the ‘favourable geometric fitting’ between the component molecules. As a result, they are labile enough to be broken down easily in the flowing process, and hence, $\Delta \eta$ turns to be negative.

The compositional variations of dynamic viscosity, $\eta$ for the mixtures were correlated through one parameter correlating equations given by Grunberg and Nissan [19], two-parameter Heric [20] and three parameters equation given by Ausländer equation [21]:

![Figure 1](image.png)

Figure 1. Comparison of viscosity, $\eta$ as a function of $x_2$ for the systems of NHP ($x_1$) + TN ($x_2$) (□), + OXN ($x_2$) (Δ) and + MSN ($x_2$) (o) at 298.15 K.
The Grunberg - Nissan interaction parameter ($\varepsilon$) is given by [19]

$$
\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 \varepsilon
$$

where the parameter $\varepsilon$ is proportional to the interchange energy. The two-parameter Heric equation follows as [20]

$$
\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln (x_1 M_1 + x_2 M_2) + x_1 x_2 [H_{12} + H_{21}(x_1 - x_2)]
$$

where, $H_{12}$ and $H_{21}$ are the adjustable parameters.

**Figure 2.** Comparison of deviation in viscosity, $\Delta \eta$, as a function of $x_2$ for the systems of NHP ($x_1$) + TN ($x_2$) (□), + OXN ($x_2$) (Δ) and + MSN ($x_2$) (○) at 298.15 K.
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The Ausländer equation [21] depends on three parameters representing binary interactions:

\[
\eta = \frac{x_1 \eta_1(x_1 + B_{12}x_2) + x_2 \eta_2 A_{21}(x_1 + B_{21}x_2)}{x_1(x_1 + B_{12}x_2) + x_2 A_{21}(x_1 + B_{21}x_2)} \tag{8}
\]

Here, \( B_{12}, B_{21} \) and \( A_{21} \) are the adjustable parameters. All the values of the parameter for NHP + TN, NHP + OXN and NHP + MSN mixtures at 298.15 K are given in Table 4 along with the percentage standard deviations.

Table 4. Adjustable parameters and standard deviation of several semi-empirical equations

| Equation                      | NHP(\(x_1\))+TN(\(x_2\)) | NHP(\(x_1\))+OXN(\(x_2\)) | NHP(\(x_1\))+MSN(\(x_2\)) |
|-------------------------------|-----------------------------|-----------------------------|-----------------------------|
| Grunberg-Nissan               | \( \varepsilon = -0.3410 \) | \( \varepsilon = -0.3461 \) | \( \varepsilon = -0.1746 \) |
|                               | \( \sigma = 0.0024 \)      | \( \sigma = 0.0020 \)      | \( \sigma = 0.0005 \)      |
| Heric equation                | \( H_{12} = 0.3340 \)      | \( H_{12} = 0.3396 \)      | \( H_{12} = 0.1576 \)      |
|                               | \( H_{21} = 0.0706 \)      | \( H_{21} = 0.0511 \)      | \( H_{21} = 0.0074 \)      |
|                               | \( \sigma = 0.0004 \)      | \( \sigma = 0.0005 \)      | \( \sigma = 0.0005 \)      |
| Ausländer equation            | \( B_{12} = 0.3617 \)      | \( B_{12} = 0.5809 \)      | \( B_{12} = 0.8845 \)      |
|                               | \( B_{21} = 0.9195 \)      | \( B_{21} = 1.2828 \)      | \( B_{21} = 1.5370 \)      |
|                               | \( A_{21} = 0.5223 \)      | \( A_{21} = 0.6562 \)      | \( A_{21} = 0.5755 \)      |
|                               | \( \sigma = 0.0004 \)      | \( \sigma = 0.0004 \)      | \( \sigma = 0.0005 \)      |

3.3. Excess Free Energy

On the basis of the theory of absolute reaction rates [22], the excess free energies of activation \( \Delta G^{\#E} \) for viscous flow have been calculated using the equation [23, 24] :

\[
\Delta G^{\#E} = RT \left[ \ln \eta V - \sum x_i \ln (\eta_i V_i) \right] \tag{9}
\]

where \( \eta, V, \eta_i \) and \( V_i \) denote the viscosity and molar volume of the mixture and of pure components, respectively, and \( R \) and \( T \) are the gas constant and the
temperature of the measured property, respectively. Fig.3 represents the comparative diagram of $\Delta G^{\#E}$ against $x_2$ at 298.15 K.

The excess free energy of activation, $\Delta G^{\#E}$, has a similar function behaviour as viscosity deviations. When they are negative, it leads to suggest that irrespective of volume expansion and contraction, all the following species surpass smaller energy barriers than it is expected from the additivity rules.

![Comparison of excess free energies of activation for viscous flow, $\Delta G^{\#E}$, as a function of $x_2$ for the systems of NHP ($x_1$) + TN ($x_2$) ($\Box$), + OXN ($x_2$) ($\Delta$) and + MSN ($x_2$) ($o$) at 298.15 K.](image)

**Figure 3.** Comparison of excess free energies of activation for viscous flow, $\Delta G^{\#E}$, as a function of $x_2$ for the systems of NHP ($x_1$) + TN ($x_2$) ($\Box$), + OXN ($x_2$) ($\Delta$) and + MSN ($x_2$) ($o$) at 298.15 K.
4. Conclusions

This work presents experimental viscosities of pure \textit{n}-heptane, toluene, \textit{o}-xylene and mesitylene, and those of their binary mixtures covering the whole composition range of mole fractions. It has been revealed that, while the system of NHP + TN is mainly dominated by dispersive forces, the so called ‘favourable geometry fitting’ is suggested to overpower in NHP + OXN and NHP + MSN due to the increasing number of –CH\textsubscript{3} groups in the OXN and MSN molecules.

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