Excess Thermodynamic Properties and Molecular Interactions in Binary Liquid Mixture of o-xylene and N-nonane

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Abstract: Experimentally measured data for viscosity and refractive index of (o-Xylene + n-Nonane) binary mixture are reported in this research paper for various compositions for three different temperatures at atmospheric pressure. Modified Ubbelohde viscometer and Abbe-3L Refractrometer were used for experimental measurements. Deviation in molar refraction (AR) and deviation in viscosity (Ay) w.r.t composition have been calculated from the experimental data. ‘Grunberg and Nissan’ equation and Herric’s Correlation were used to correlate the viscosity data. Excess thermodynamic properties were fitted to Redlich-Kister equation. Coefficients and standard deviations, hence obtained are reported. Variation in Excess Thermodynamic properties for the mixture have been discussed in terms of intermolecular interactions.

IndexTerms: o-Xylene, n-Nonane, deviation in molar refraction, deviation in viscosity.

I. INTRODUCTION
Experimental measurement of physical properties like viscosity and density of liquid mixtures finds use in determining thermodynamic excess properties of non-ideal solutions. These excess properties, in turn, help in understanding intermolecular interactions in the binary mixture formed at known temperature, pressure conditions. Researchers [1,2] have worked on (Alkane + substituted Benzene) binary liquid mixtures to understand the type of molecular interactions involved. In continuation to the reported earlier studies, we present the experimental data for viscosity and refractive index of (o-Xylene + n-Nonane) binary mixture at T= (293.15, 298.15, and 303.15) K and at normal atmospheric pressure. The trends of excess thermodynamic properties with composition and temperature have been reported. The possible molecular interactions too have been discussed. Nonane is used as a distillation chaser, fuel additive and in preparing organic solvents for specific utilities. It is also a component in automotive and jet fuel. Xylene is a major petrochemical produced by catalytic reforming and used in printing, rubber, and leather industries. o-Xylene is used to produce phthalic anhydride, which is a precursor to many materials, drugs and other chemicals. Xylenes are frequently used as octane enhancer in vehicles.

II. RESEARCH METHODOLOGY
2.1 Chemicals used
o-Xylene (AR grade, Loba Chemie Pvt. Ltd., Mumbai) and n-Nonane (AR grade, Himedia Laboratories Pvt. Ltd., Mumbai) were used in the study after purification. Standard procedures were used to purify the chemicals. A comparison of measured and values reported in literature for refractive indices and viscosities was done as purity check (Table I).

2.2 Apparatus and procedure
Modified Ubbelohde viscometer [3] was used for the measurement of viscosity of pure compounds and the samples of varying composition of the binary mixture. Distilled benzene and cyclohexane were used for its calibration at atleast three different temperatures. Using the following equation, the values of the constants (A and B) were determined for the viscometer:

\[ \eta/\rho = At + B/t \]

where, 
\( \eta \) (kinematic viscosity) = \( \eta/\rho \),

\( t \) = average time,

Before each reading, it was ensured that the viscometer was washed with water several times and then with acetone. Finally, it was dried under vacuum. A circulating-type cryostat [4] (type MK70, MLW, Germany) maintained at a temperature with in ± 0.02 K, earlier used by our team, was used to maintain the temperature of each sample Abbe-3L refractometer (designed by Bausch and Lomb) was used to measure refractive index of equilibrated mixtures. Gill et al. have earlier discussed the procedure adopted for measurements as “Refractive index readings were taken on samples with sufficient time allowed for the sample to come to thermal equilibrium at the required temperature with the help of a circulating type cryostat (Type MK70, MLW, Germany) maintained at a temperature with in ± 0.02 K”.

III. DATA TREATMENT
Molar Refraction \( R_m \) was calculated by using the experimentally determined values of refractive index with the help of Lorentz-Lorenz equation [5]:

\[ R_m = \frac{[n_0^2 - 1]}{[n_0^2 + 2]} \times \sum x_i M_i \times \rho_m \] (1)

Deviation in molar refraction was calculated using the following relation:

\[ \Delta R = R_m - \sum x_i R_i \] (2)

where, \( \Delta R \) is the deviation in molar refraction, \( R_m \) and \( R_i \) is the molar refraction of mixture and pure component ‘i’ respectively, \( n_0 \) is the refractive index, \( x_i \) and \( M_i \) are mole fraction and molecular mass of component ‘i’ respectively and \( \rho_m \) is the density of the mixture.

Density values [6] considered for molar refraction calculation were obtained from previous study made by the authors.
Following equation was used to calculate deviation in viscosity, $\Delta \eta$:

$$\Delta \eta = \eta_m - (x_1 \eta_1 + x_2 \eta_2) \quad (3)$$

where, $\eta_m$, $\eta_1$, and $\eta_2$ are the viscosities of mixture, $o$-Xylene and $n$-Nonane respectively. Table II, III and IV display the experimentally measured values of viscosity, refractive index as well as excess properties i.e. deviation in Molar Refraction and deviation in Viscosity for the binary mixture of $o$-Xylene + $n$-Nonane over the entire composition range at 293.15 K, 298.15K and 303.15K respectively.

Deviation in Molar Refraction ($\Delta R$) and deviation in viscosity ($\Delta \eta$) were fitted to Redlich-Kister type equation [7]:

$$A = x_1 x_2 \sum_{j=1}^{n} A_{j-1} (x_1 - x_2)^{j-1} \quad (4)$$

where,

$A$ is the property under consideration, $A_{j-1}$ is the polynomial coefficient, $x_1, x_2$ refers to the mole fractions of component 1 and 2 respectively and $n$ is the polynomial degree.

The standard deviation ($\sigma$) was calculated using the following expression:

$$\sigma(X) = \left[ \frac{\sum (X_{exp} - X_{cal})^2}{N - n} \right]^{1/2} \quad (5)$$

where, $X$ is the property under consideration, $X_{exp}, X_{cal}$ are the experimental and calculated values respectively, $N$ is the number of data points and $n$ is the number of coefficients.

Coefficients ($A_k$) of the Redlich-Kister Equation and Standard Deviation ($\sigma$) for both the excess properties studied i.e. deviation in Molar Refraction and deviation in Viscosity for the binary mixture of $o$-Xylene + $n$-Nonane are listed in Table V.

The experimental viscosity data were fitted to the following semi-empirical relations:

1. Herric’s equation:

Kinematic viscosities were fitted to Herric’s Correlation [8] and the parameters were determined.

$$\ln V = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 [\alpha_{12} + \alpha'_{12} (x_1 - x_2)] - \ln M_{mix} + x_1 \ln M_1 + x_2 \ln M_2$$

where, $\alpha_{12}$ and $\alpha'_{21}$ are interaction parameters of Herric’s correlation.

2. Grunberg and Nissan equation:

Dynamic viscosities were fitted to Grunberg and Nissan [9] equation.

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

where, $\eta$ is the viscosity of mixture; $\eta_1$ and $\eta_2$ are the viscosity of pure components 1 and 2 respectively; $x_1, x_2$ refers to the mole fractions of pure components 1 and 2 respectively; $d$ is the parameter.

The evaluated interaction parameters of Herric’s correlation, Grunberg –Nissan equation are presented in Table VI and VII respectively.

### Table I Refractive index and viscosity data at 293.15 K

| Component | $n_D$ | $\eta$ (cP) |
|-----------|-------|--------------|
|           | Exp.  | Lit.         | Exp.  | Lit.         |
| $o$-Xylene| 1.5058| 1.5054       | 0.8102| 0.810        |
| $n$-Nonane| 1.4064| 1.4057       | 0.7139| 0.714        |

### Table II Experimental data and calculated excess properties of samples of varying composition in ($o$-Xylene + $n$-Nonane) binary mixture at 293.15K

| $x_1$ | $n_D$ | $\eta$ (cP) | $\Delta R$ (cm$^3$/mol) | $\Delta \eta$ (cP) |
|-------|-------|-------------|--------------------------|-------------------|
| 0.0000| 1.406430| 0.7139      | 0.0000                   | 0.0000            |
| 0.0620| 1.412440| 0.7160      | 0.2435                   | -0.0039           |
| 0.1298| 1.420464| 0.7202      | 0.4365                   | -0.0062           |
| 0.2371| 1.427516| 0.7276      | 0.6411                   | -0.0092           |
| 0.3438| 1.438560| 0.7355      | 0.7656                   | -0.0115           |
| 0.4220| 1.447582| 0.7422      | 0.8227                   | -0.0123           |
| 0.5502| 1.457650| 0.7541      | 0.7976                   | -0.0128           |
|       |        |             | 0.6255                   | 0.7476            |
|       |        |             | 0.7342                   | 0.6009            |
|       |        |             | 0.8425                   | 0.3841            |
|       |        |             | 0.9191                   | 0.2569            |
|       |        |             | 0.9614                   | 0.0988            |
|       |        |             | 1.0000                   | 0.0000            |
Table III
Experimental data and calculated excess properties of samples of varying composition in (o-Xylene + n-Nonane) binary mixture at 298.15K

| $x_1$ | $n_o$  | $\eta$ (cP) | $\Delta R$ (cm$^3$ .mole$^{-1}$) | $\Delta \eta$ (cP) |
|-------|--------|-------------|---------------------------------|-------------------|
| 0.0000| 1.403394| 0.6606      | 0.0000                          | 0.0000            |
| 0.0620| 1.409420| 0.6644      | 0.2181                          | -0.0022           |
| 0.1298| 1.415442| 0.6684      | 0.3845                          | -0.0046           |
| 0.2371| 1.425492| 0.6759      | 0.5398                          | -0.0074           |
| 0.3438| 1.434530| 0.6840      | 0.6303                          | -0.0096           |
| 0.4220| 1.443580| 0.6908      | 0.6761                          | -0.0103           |
| 0.5502| 1.453630| 0.7026      | 0.6808                          | -0.0108           |
| 0.6255| 1.462660| 0.7106      | 0.6404                          | -0.0101           |
| 0.7342| 1.473710| 0.7225      | 0.5303                          | -0.0086           |
| 0.8425| 1.483756| 0.7356      | 0.3038                          | -0.0059           |
| 0.9191| 1.493790| 0.7441      | 0.1467                          | -0.0047           |
| 0.9614| 1.497816| 0.7509      | 0.0594                          | -0.0020           |
| 1.0000| 1.502830| 0.7566      | 0.0000                          | 0.0000            |

Table IV
Experimental data and calculated excess properties of samples of varying composition in (o-Xylene + n-Nonane) binary mixture at 303.15 K

| $x_1$ | $n_o$  | $\eta$ (cP) | $\Delta R$ (cm$^3$ .mole$^{-1}$) | $\Delta \eta$ (cP) |
|-------|--------|-------------|---------------------------------|-------------------|
| 0.0000| 1.401380| 0.6187      | 0.0000                          | 0.0000            |
| 0.0620| 1.407416| 0.6228      | 0.1583                          | -0.0014           |

Table V
I
Interaction parameters of Herric’s Correlation and standard deviation

| $T(K)$     | $\alpha_{12}$ | $\alpha_{21}$ | $\sigma$ |
|-----------|----------------|----------------|----------|
| 293.15    | 0.0918         | 0.0160         | 0.0002   |
| 298.15    | 0.0506         | 0.0088         | 0.0007   |
| 303.15    | 0.0385         | 0.0068         | 0.0003   |

Table VI
Grunberg-Nissan parameter and standard deviation

| $T(K)$     | $d$            | $\sigma$ |
|-----------|----------------|----------|
| 293.15    | -0.0110        | 0.0013   |
| 298.15    | -0.0528        | 0.0004   |
| 303.15    | -0.0497        | 0.0003   |
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Table V

| EXCESS PROPERTY | T(K)  | \(A_0\)  | \(A_1\)  | \(A_2\)  | \(A_3\)  | \(\sigma\) |
|-----------------|-------|---------|---------|---------|---------|---------|
| \(\Delta R\) (cm\(^3\)mol\(^{-1}\)) | 293.15 | 3.2343  | -0.2512 | 0.2352  | -0.7422 | 0.0096  |
|                 | 298.15 | 2.7667  | -0.0127 | 0.0129  | -1.4033 | 0.0088  |
|                 | 303.15 | 2.3467  | -0.0825 | 0.0533  | -1.0022 | 0.0078  |
| \(\Delta \eta\) (mPa.s) | 293.15 | -0.0027 | -0.0277 | 0.0017  | 0.0281  | 0.0111  |
|                 | 298.15 | -0.0012 | -0.0521 | 0.0640  | 0.0145  | 0.0119  |
|                 | 303.15 | -0.0013 | -0.0175 | 0.0163  | 0.0362  | 0.0070  |

IV. RESULTS AND DISCUSSION

Refractive index \((n_D)\) of binary mixture was measured at three different temperatures. Refractive index decreases with increase in temperature as evident from reported experimental data in Table II, III and IV. It implies that at higher temperature, liquid mixture becomes less dense and less viscous, causing the light to travel faster in that medium. From Fig.1, it was observed that \(\Delta R > 0\) for samples of all compositions at \(T= (293.15, 298.15, \text{and} \ 303.15)\) K. Another observation is that with increase in temperature, deviation in molar refraction decreases.

![Fig. 1: Deviation in molar refraction \((\Delta R)\) vs. mole fraction of \(o\)-Xylene \((x_1)\) at 293.15(▲), 298.15K (♦) and 303.15 K (■)](image)

Viscosity data were obtained experimentally for all listed samples of the binary mixture at three different temperatures. From the experimental data presented in Table II, III and IV, it was observed that with increase in temperature, viscosity of mixture decreases. Fig. 2 indicates that \(\Delta \eta < 0\) for samples of all compositions at \(T= (293.15, 298.15, \text{and} \ 303.15)\) K. It suggests that the intermolecular interaction becomes weaker on mixing of components, also indicating that the dispersion forces are predominant in these mixtures.

![Fig. 2: Deviation in Viscosity \((\Delta \eta)\) vs. mole fraction of \(o\)-Xylene \((x_1)\) at 293.15(▲), 298.15K (♦) and 303.15 K (■)](image)

IV. CONCLUSION

Negative \(\Delta \eta\) values account for dispersive forces in the binary mixture of \(o\)-Xylene with \(n\)-Nonane and the trends are supported by earlier studies on similar binary mixtures [10]. The viscosity data of the liquid mixture were correlated using Grunberg-Nissan equation and Herric’s correlation.
Small standard deviation values (Table VI and VII) indicate the suitability of these equations to represent the viscosity of the binary mixture.

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