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

B. K. Gill, Minakshi, V. K. Ratttan

***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 Ubbelholde viscometer and Abbe-3L Refractometer were used for experimental measurements. Deviation in molar refraction (ΔR) and deviation in viscosity (Δη) 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.

Revised Manuscript Received on April 30, 2020.
***** Correspondence Author
B. K. Gill[*], Dr. SSBUICET, Panjab University, Chandigarh, INDIA. E-mail: bkg-72@hotmail.com
Minakshi, Dr. SSBUICET, PU, Chandigarh, INDIA.
V. K. Ratttan, Dr. SSBUICET, PU, Chandigarh, INDIA.

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,
ν (kinematic viscosity) = η/ρ,
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]:

$$\mathbf{R_m} = \frac{[n_D^2-1]}{[n_D^2+2]} \cdot \frac{\sum x_i M_i}{\rho_m} \quad (1)$$

Deviation in molar refraction was calculated using the following relation:

$$\Delta R = R_m - \sum x_i R_i \quad (2)$$

where, ΔR is the deviation in molar refraction, R_m and R_i is the molar refraction of mixture and pure component 'i' respectively, n_D is the refractive index,

x_i and M_i are mole fraction and molecular mass of component 'i' respectively and ρ_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, η_m, η_1 and η_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 (ΔR) and deviation in viscosity ($\Delta\eta$) were fitted to Redlich-Kister type equation [7]:

$$A = x_1x_2\sum_{j=1}^{n} A_{j-1}\,(x_1 - x_2)^{j-1} \quad (4)$$

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 (σ) 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 (σ) forboth 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.

$$\ln\nu = x_1\ln\nu_1 + x_2\ln\nu_2 + x_1x_2[\alpha_{12} + \alpha'_{12}(x_1 - x_2)] - \ln M_{mix} + x_1\ln M_1 + x_2\ln M_2 \quad (6)$$

where, α_{12} and α_{21} are interaction parameters of Herric's correlation.

2. Grunberg and Nissan equation:

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

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2 \quad (7)$$

where, η 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 Exp.	n_D Lit.	η (cP) Exp.	η (cP) 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	η (cP)	ΔR ($cm^3.mole^{-1}$)	$\Delta\eta$ (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	1.464680	0.7619	0.7476	-0.0122
0.7342	1.474706	0.7738	0.6009	-0.0108
0.8425	1.486764	0.7846	0.3841	-0.0075
0.9191	1.495800	0.7971	0.2569	-0.0053
0.9614	1.499820	0.8032	0.0988	-0.0033
1.0000	1.505846	0.8102	0.0000	0.0000

International Journal of Innovative Technology and Exploring Engineering (IJITEE)
ISSN: 2278-3075 (Online), Volume-9 Issue-6, April 2020

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_D	η (cP)	ΔR ($cm^3.mole^{-1}$)	$\Delta\eta$ (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_D	η (cP)	ΔR ($cm^3.mole^{-1}$)	$\Delta\eta$ (cP)
0.0000	1.401380	0.6187	0.0000	0.0000
0.0620	1.407416	0.6228	0.1583	-0.0014
0.1298	1.413440	0.6264	0.3165	-0.0039
0.2371	1.422488	0.6335	0.4674	-0.0064
0.3438	1.430530	0.6407	0.5489	-0.0087
0.4220	1.440570	0.6468	0.5747	-0.0096
0.5502	1.450610	0.6580	0.5704	-0.0098
0.6255	1.460658	0.6651	0.5279	-0.0095
0.7342	1.470700	0.6765	0.4295	-0.0078
0.8425	1.480751	0.6885	0.2716	-0.0054
0.9191	1.490782	0.6973	0.1298	-0.0034
0.9614	1.494816	0.7028	0.0540	-0.0018
1.0000	1.500820	0.7080	0.0000	0.0000

Table VI
Interaction parameters of Herric's Correlation and standard deviation

T(K)	α_{12}	α_{21}	σ
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 VII
Grunberg-Nissan parameter and standard deviation

T(K)	d	σ
293.15	--0.0110	0.0013
298.15	-0.0528	0.0004
303.15	-0.0497	0.0003

Table V Coefficients of the Redlich-Kister Equation and Standard Deviations (σ) for the excess properties

EXCESS PROPERTY	T(K)	A_0	A_1	A_2	A_3	σ
ΔR (cm^3mol^{-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, and 303.15) K. Another observation is that with increase in temperature, deviation in molar refraction decreases.

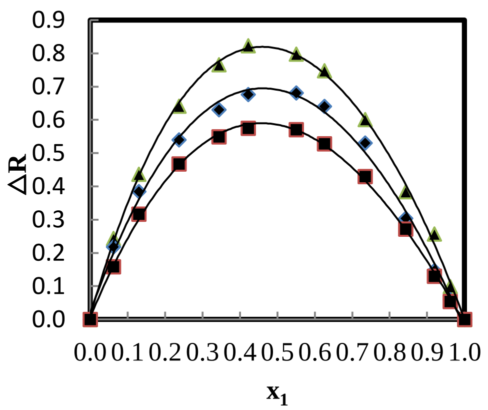

Fig. 1: Deviation in molar refraction (ΔR) vs. mole fraction of *o*-Xylene (x_1) at 293.15(▲), 298.15K (♦) and 303.15 K (■)

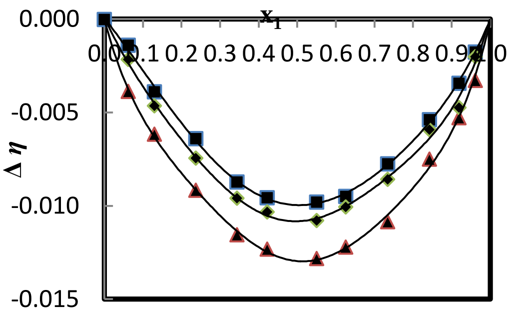

Fig. 2: Deviation in Viscosity ($\Delta\eta$) vs. mole fraction of *o*-Xylene (x_1) at 293.15(▲), 298.15K (♦) and 303.15 K (■)

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, 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.

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.

REFERENCES

1. Y.Changsheng, M. A. Peisheng, and Z. Qing, "Excess molar volumes and viscosities of Binary Mixtures of p- Xylene with Cyclohexane, n-Heptane, n- Octane, Sulfolane, N- Methyl-2-pyrrolidone and Acetic Acid at 303.15 K and 323.15 K," Chinese Journal of Chemical Engineering, Vol.12(5), 2004, pp. 700-706.
2. H, Iloukhani, M. R. Sameti and J. B, Parsa , "Excess molar volumes and dynamic viscosities for binary mixtures of toluene + n-alkanes (C5–C10) at T = 298.15 K – Comparison with Prigogine–Flory–Patterson theory," Journal of Chemical Thermodynamics,Vol 38, 2006, pp 975-982.
3. B. K. Gill, R. Bhanoteand V. K. Rattan, "Excess Thermodynamic properties of a binary liquid mixture of Isopropylbenzene and N, N-Dimethylformamide at T= 293.15 K, 303.15 K and 313.15 K," Journal of Emerging Technologies and Innovative Research, Vol. 5, 2018, pp. 222-232.
4. B. K. Gill, V. K. Rattan and S. Kapoor, "Vapour-Liquid Equilibrium Data for N - Methylacetamide and N, N- Dimethylformamide with Cumene at 97.3 kPa,"Journal of Chemical and Engineering Data, Vol. 54, 2009, pp.1175-1178.
5. B. K. Gill, H. Sharma and V. K. Rattan, "Refractive Index, Excess Molar Volume and Viscometric study of binary liquid mixture of Morpholine with Cumene at 298.15 K, 303.15 K and 308.15 K," International Journal of Chemical and Molecular Engineering, Vol.10, 2016, pp. 325-330.

6. Minakshi, Excess Thermodynamic properties of Binary Liquid mixtures of *n*-Nonane with*o*-Xylene and *p*-Xylene at 293.15, 298.15 and 303.15 K , M.E. Thesis(Aug, 2015), Panjab University, Chandigarh.
7. V. K. Rattan, S. Singh andB. P. S.Sethi , "Viscosities, densities, and ultrasonic velocities of binary mixtures of ethylbenzene with ethanol, 1-propanol, and 1-butanol at (298.15 AND 308.15) K," Journal of Chemical and Engineering Data, Vol. 49, 2004,pp.1074-1077.
8. L. Grunberg and A. H.Nissan, "Mixture law for viscosity,"Nature, 164, 1949, 799-800.
9. J. A. Riddick, W. B. Bunger and T. K. Sakano, *Organic Solvents: Physical Properties and Methods of Purification*, (John Wiley and Sons, New York) 1986.
10. C. Yang, W. Xu and P. Ma,"Thermodynamic properties of binary mixtures of p-xylene with cyclohexane, heptane, octane, and n-methyl-2-pyrrolidone at several temperatures,"Journal of Chemical and Engineering Data, 49, 2004, pp.1794-1801.

AUTHOR'S PROFILE

Dr. B. K. Gill, Dr. Shanti Swaroop Bhatnagar University Institute of Chemical Engineering and Technology, Panjab University, Chandigarh, India.

Minakshi, PG research scholar**,** Dr. SSBUICET, Panjab University, Chandigarh, India. Presently doing Ph.D.

Prof. V.K. Ratttan, Dr. SSBUICET, Panjab University, Chandigarh, India. Presently serving as Vice Chancellor, GNA University. Phagwara.