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

Md. Kamrul Hossain[1], M. Abdur Rahaman[2] and Shamim Akhtar[1*]

[1]Department of Chemistry, University of Chittagong, Chittagong-4331, Bangladesh.
[2]Department of Chemistry, Mawlana Bhashani Science and Technology University, Tangail-1902, Bangladesh.
*Corresponding Author: shamim3332000@yahoo.com.

Abstract

The viscosities, η , 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 η 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.*

বিশুদ্ধ n-হেপ্টেন, টলুইন, o-জাইলিন, মেসিটাইলিন এবং তাদের বাইনারী মিশ্রনের সান্দ্রতা ২৯৮.১৫K তাপমাত্রায় নির্ণয় করা হয়েছে। পরীক্ষার ফলাফল ব্যবহার করে সান্দ্রতার বিচ্যুতি গণণা করা হয়। ঘণমাত্রা নির্ভরশীল সান্দ্রতাকে সমন্বয় করা হয়েছে পলিনমিয়াল অভিব্যক্তি দ্বারা, যেখানে সান্দ্রতার বিচ্যুতিকে যুক্ত করা হয়েছে Redlich-Kister অভিব্যক্তি দ্বারা । পরন্ত, এই বাইনারী মিশ্রনগুলোর গিবসের অতিরিক্ত সক্রিয়ন শক্তির মানগুলো, $\Delta G^{\#E}$, নির্ণয় করা হয়েছে। বাইনারী সিস্টেমের সান্দ্রতা পরিমাপ Grunberg- Nissan থ্রি বডি এবং ফোর বডি McAllister অভিব্যক্তির সাথে সম্পর্কযুক্ত করা হয়েছে। সব সিস্টেমের সমগ্র পরিসীমায় $\Delta \eta$ এর মান একক লোব হিসেবে অ্যারোমেটিক হাইড্রোকার্বনের 0.6 মোল ভগ্নাংশে ঋনাত্নক পাওয়া গেছে। যেখানে ডিসপারসিভ বল n-হেপ্টেন + টলুইন সিস্টেমে আধিপত্য বিস্তার করে সেখানে অন্যান্য দুটি সিস্টেমে অ্যারোমেটিক হাইড্রোকার্বনে -CH_3 গ্রুপ বৃদ্ধির কারণে অনুকূল জ্যামিতিক ফিটিং প্রাধান্য পায়।

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_5-C_{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_6-C_{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 η. 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 η 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, η of pure liquids at 298.15 K.

Sample	η /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, η, 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, η values were fitted to a four-degree polynomial equation of the form:

$$\eta/mPa\cdot S = \sum_{i=0}^{n} a_i x_2^i \tag{1}$$

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

$$AAD\% = \frac{1}{N_p} \sum_{i=1}^{N_p} \left[\frac{\eta_i^{exp} - \eta_i^{cal}}{\eta_i^{exp}} \right] \times 100 \tag{2}$$

where, N_p is the number of experimental points, and η_i^{exp} and η_i^{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 η against x_2 of the three systems at 298.15 K. The η of pure liquids varies in the order: OXN > MSN > TN > NHP. For their binary mixtures, η 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 η, the viscosity deviations $\Delta\eta$ were calculated using equations as in [11, 12]:

$$\Delta\eta = \eta - \eta_1 x_1 - \eta_2 x_2 \tag{3}$$

where, η is the viscosity of solution, η_1 and η_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]:

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

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

The standard deviation, σ, followed the equation:

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

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 σ are as shown in Table 3. Fig. 2 depicts the variation of $\Delta\eta$ with the mole fraction x_2. The deviatin 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 $x_2\sim0.6$. At a particular temperature, $\Delta\eta$ variation followed the order: NHP + OXN > + TN > + MSN.

Table 2. Viscosities, η (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	η	$\Delta\eta$	x_2	η	$\Delta\eta$	x_2	η	$\Delta\eta$
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, η (mPa.s) and AAD% and fitting coefficients, A_i and standard deviation, σ 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	σ
					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 π -electrons below and above the rings. With increasing number of $-CH_3$ substituents at different positions further enhance their π -electron density. So that, forces like dipole-dipole, dipole - quardrapole 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 results, 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, η 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]:
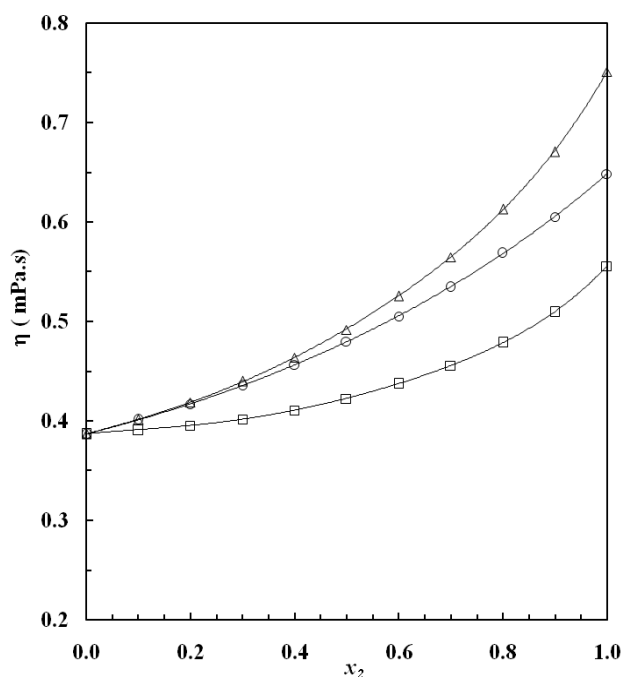
Figure 1. Comparison of viscosity, η as a function of x_2 for the systems of NHP (x_1) + TN (x_2) (□), + OXN (x_2) (Δ) and + MSN (x_2) (o) at 298.15 K.
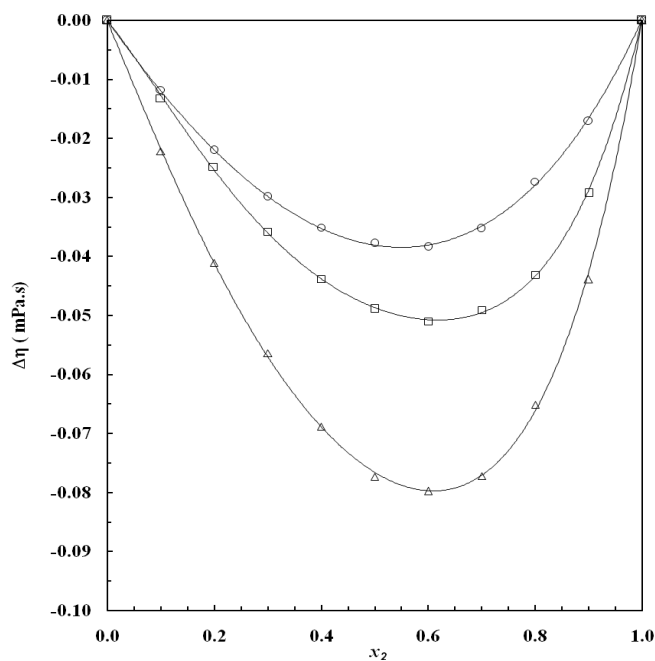
The Grunberg - Nissan interaction parameter (ε) is given by [19]

$$ln\,\eta = x_1\,ln\,\eta_1 + x_2\,ln\,\eta_2 + x_1 x_2 \varepsilon \qquad (6)$$

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

$$ln\,\eta = x_1\,ln\,\eta_1 + x_2\,ln\,\eta_2 + x_1\,ln\,M_1 + x_2\,ln\,M_2 - ln(\,x_1 M_1 + x_2 M_2\,) + x_1 x_2 \{\,H_{12} + H_{21}(\,x_1 - x_2\,)\} \qquad (7)$$

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) ($\square$), + OXN (x_2) (Δ) and + MSN (x_2) (o) at 298.15 K.

The Ausländer equation [21] depends on three parameters representing binary interactions:

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

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

|	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	H12=-0.3340	H12=-0.3396	H12=-0.1576
	H21=0.0706	H21=0.0511	H21=0.0074
	$\sigma = 0.0004$	$\sigma = 0.0005$	$\sigma = 0.0005$
Ausländer equation	B12=0.3617	B12=0.5809	B12=0.8845
	B21=0.9195	B21=1.2828	B21=1.5370
	A21=0.5223	A21=0.6562	A21=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 η, V, η_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.
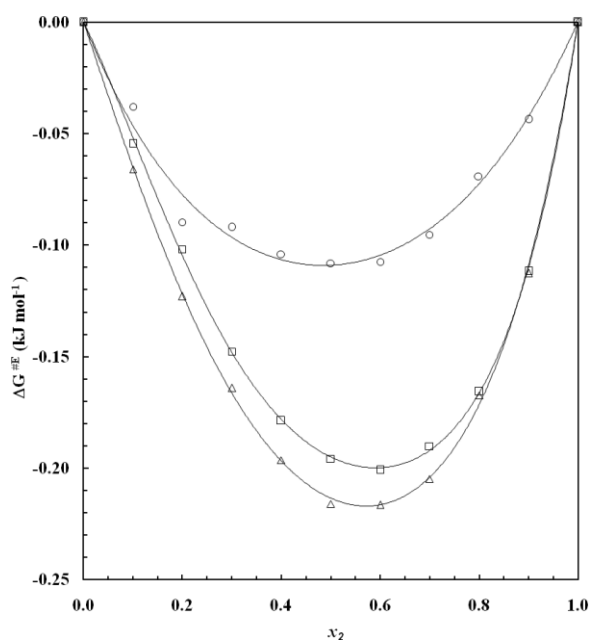
Figure 3. Comparison of excess free energies of activation for viscous flow, $\Delta G^{\#E}$, as a function of x_2 for the systems of NHP (x_1) + TN (x_2) ($\square$), + OXN (x_2) (Δ) and + MSN (x_2) (o) at 298.15 K.

4. Conclusions

This work presents experimental viscosities of pure *n*-heptane, toluene, *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 $-CH_3$ groups in the OXN and MSN molecules.

References

1. J. N. Nayak, M. I. Aralaguppi and T. M. Aminabhavi., *J. Chem. Eng. Data,* 2003, **48**, 1152.

2. E Pérez, M. Cardoso, A. M. Mainar, J. I. Pardo and J. S. Urieta, *J. Chem. Eng. Data,* 2003, **48**, 1306.

3. H. Iloukhani, M. Rezaei-Sameti, J.Basiri-Parsa, *J. Chem. Thermodyn.,* 2006, **38**, 975.

4. M. A Rahaman, M. S. I. Aziz, S. Akhtar, *J. Mol. Liq.,* 2011, **162**, 26.

5. K. Lal, N. Tripathi and G. P. Dubey, *J. Chem. Eng. Data,* 2000, **45**, 961.

6. T. M. Aminabhavi and B. V. Patil, *J. Chem. Eng. Data,* 1997, **42**, 641.

7. A. K. Nain, *Phys. Chem. Liq.,* 2007, **45**, 371.

8. S. C. Bhatia, R. Rani, R. Bhatia, *J. Mol. Liq.,* 2011, **159**, 132.

9. M. I. Aralaguppi, T. M. Aminabhavi, S. B. Harogoppad, R. H. Balundgi, *J. Chem. Eng. Data,* 1992, **37**, 298.

10. M. A. Hernandez-Galvan, F. Garcıa-Sanchez, R. Macıas-Salinas, *Fluid Phase Equilibria,* 2007, **262**, 51.

11. C. Yang, P. Ma, Q. Zhou, *J. Chem. Eng. Data,* 2004, **49**, 881.

12. G. Li, H. Chi, Y. Guo, W. Fang and S. Hu, *J. Chem. Eng. Data,* 2013, **58**, 3078.

13. O.J. Redlich and A.T. Kister, *Ind. Eng. Chem.,* 1948, **40**, 345.

14. S. Singh, B. P. S. Sethi, R. C. Katyal and V. K. Rattan., *J. Chem. Eng. Data,* 2005, **50**, 125.

15. S. Varshney and M. Singh, *J. Chem. Eng. Data,* 2006, **51**, 1136.

16. K.J. Han, J.H. Oh and So-Jin Park, *J. Chem. Eng. Data,* 2006, **51**, 1339.

17. D. Agarwal and M. Singh, *J. Chem. Eng. Data,* 2004, **49**, 1218.

18. M. Hasan, A. B. Sawant, R. B. Sawant, P. G. Loke, *J. Chem. Thermodyn.,* 2011, **43**, 1389.

19. L. Grunberg and A.H. Nissan, *Nature,* 1949, **164**,799.

20. E.L. Heric, *J. Chem. Eng. Data,* 1966, **11**, 66.

21. G. Auslander, *Br. Chem. Eng.,* 1965, **10**, 196.

22. S. Glasstone et al., The Theory of Rate Process, McGraw-Hill: New York, 1941, p. 345.

23. S. L. Oswal, K. D. Prajapati, P. Oswal, N. Y. Ghael, S. P. Ijardar, *J. Mol. Liq.,* 2005, **116,** 73.

24. N. V. Sastry, S. R. Patel, S. S. Soni, *J. Mol. Liq.,* 2013, **183**, 102.