Dielectric Relaxation Studies of Some Aromatic Hydrocarbons and Their Naphthene Mixtures

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The frequency dependence of complex dielectric constant ε^*, and the loss factor 'tan δ' for xylene isomers (para, meta and ortho-xylene), pure naphthene and 50% mixture of naphthene have been studied from 100 KHz to 100 MHz. The dielectric relaxation process has also been studied. The data has been analyzed in terms of Cole-Cole and Higasi type distribution. The results obtained for xylene isomers are in agreement with, Cole-Cole type of semicircle representation. Relaxation time 'τ' has been calculated from viscosity data obtained from Happlier apparatus, at four different temperatures. To study the effective relaxation mechanism of molecules in polar solute and solvent and their mixtures, along with the given values of heat of absorption of these liquids, Hartshorn and Ward apparatus has been used for the measurement of dielectric parameters. The results support our assumption that the dielectric absorption in xylene isomers is due to overall molecular rotation.

Key words: Dielectric constant, Relaxation time, Viscosity, Loss factor.

Introduction

Most polar liquids show broad absorption, which arises due to the orientation of the polar molecules under high A.C. field. The general relationship of the dielectric constant ε' and the loss factor ε'' of a polar liquid, possessing a single relaxation time 'τ' may be expressed as (Debye 1961):

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) / (1 + \omega^2 \tau^2) \quad \text{...............................} \quad (1)$$

$$\varepsilon'' = \omega\tau(\varepsilon_s - \varepsilon\tau) / (1 + \omega^2 \tau^2) \quad \text{...............................} \quad (2)$$

where ε_s is the low frequency dielectric constant (static), and ε_∞ is the dielectric constant at very high frequency. As obvious from above equations, the ε' decreases between ε_s to ε_∞. At higher frequencies, most of the decrease in ε' occurs within hundreds of frequency. The transition from high to low ε' occurs at $\omega_0 = 1/\tau$ and tends to be broader than that for reasonance absorption (Jackson and Poweless 1950). Unlike the resonance absorption, ε' which has no maxima and minima on either side of the drop at ω_0, there is, however, a strong energy absorption term in ε'' and is peaked at t^{-1}. The effective dielectric relaxation time of a polar solute molecules varies markedly from the value for an equivalent rigid structure (Lashmi and Narayana 1960). These molecules contain internal relaxation mechanism, arising from the rotating groups exist in some liquids (Reid and Hough 1957). This is a cooperative phenomenon (Hill 1954). The dielectric orientation is closely related to the structural breakup of these groups (McDuffie and Litovite 1962) and this breakup is a necessary condition for dipole orientation (Meyer and Morrison 1991).

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The influence of viscosity of the medium upon the relaxation time 'τ' and the adequacy of the Hill treatment of this factor should also be considered for the calculation of relaxation time 'τ' (Singh and Sharma 1993). In the frequency domain, (Fang 1965) the relaxation function is a complex function of frequency, the real part is called the dispersion and the imaginary component is absorption (Jayaraj and Sobhanadri 1980). For the analysis of the dielectric relaxation data in the frequency domain, a very convenient representation is in the form of Cole-Cole diagram.

The xylene isomers, used in this study, characterised by triply saturated six member ring have the properties of subtituents by saturated carbon atoms. Dielectric relaxation studies of some aromatic hydrocarbons and their naphthene mixtures have been carried out and reported in this paper. An analysis and interpretation of some experimental data by the use of a function for the distribution of relaxation time have also been described.

Experimental

The dielectric properties, such as complex dielectric constant ε^*, the loss factor tan δ and the relaxation time 'τ' for the xylene isomers (para, meta and ortho xylene), 50 percent naphthene and p-xylene mixture and pure naphthene have been measured from 100 KHz, to 100 MHz, at 303.5 to 318.5 K, using Hartshorn and Ward apparatus. By employing the method of capacitance variation in a resonant circuit and a square law thermoinic voltmeter being employed as reasonance indicator, both the permitivity ε' and tan δ are obtained as a

ratio of the capacitance readings. This equipment includes two interchangeable high frequency oscillator units. The general characteristics and the limits of accuracy of measurements were ± 5% for loss tangent and the ± 1% for dielectric constant (both real and imaginary parts) ε' and ε''.

For the calculation of relaxation time of the molecules in liquids the viscosity of the above liquids have been measured at four temperatures for each solvent by "Happlier Falling Ball Viscometer" (Vogel 1989) from the rate of falling sphere using the following formula:

$$\eta = KT (ds - dl) dt \dots\dots\dots (3)$$

where K is Boltzman constant, T is the temperature in K, ds and dl are the densities (in g cm^3) of solid ball and liquid sample, used in apparatus and dt is the change in falling time. The apparatus satisfactorily measures the viscosity η of liquids and gases. The instrument was calibrated against a standard solution and was accurate to ± 5%. For the comparison, the heat of vaporization of five samples has been included in the Table 1 (Reymond Kirk 1993).

Chemicals. Pure samples (Analar grade E. Merck) of the three xylene isomers, i.e. meta, para and ortho xylene were used. The pure naphthene was obtained from M/s Hydrocarbon Development Institute, Karachi. The liquid samples, used in this experiments, have been subjected to proper distillation before use and their purity was checked by Thin Layer Chromatography (TLC).

Measurements & calculations. Permitivity ε' is measured as a ratio of two capacitances C and C_o,

$$\varepsilon' = C/C_o \dots\dots\dots\dots (4)$$

the loss tangent is measured by:

$$\tan \delta = \Delta C_i - \Delta C_o / 2C_s \dots\dots\dots (5)$$

within the limits of error ΔC_i is the change in Vernier readings with sample and ΔC_o without sample, and C_s is the sample capacitance. Therefore, practically.

$$\tan \delta = \varepsilon'' / \varepsilon' \dots\dots\dots\dots (6)$$

Table 2, 3, 4 and 5 show the values of ε'', ε' and $\tan \delta$ between frequencies of 0.1MHz to 100 MHz which have been measured by Frequency Counter (TRIO-Model 203A, Japan) at room temperature. Table 1 shows the observed and literature values of the following parameters at four different temperatures, 303.5K, 308.5K, 313.5Kand 318.5K at a frequency of 0.1MHz:

1) Heat of vapourization in cal g^{-1}; 2) Density 'd' in g cm^{-3}; 3) Viscosity 'η' in centipoise; 4) Apparent values of dielectric constant; 5) Calculated values of relaxation time in sec.

The relaxation time 'τ' is calculated from the pure liquids and xylene isomers. According to the treatment of the Hill (1984) and Debye (1961), the relaxation time in seconds is calculated from the below equation within the limits of experimental errors:

$$\tau = 4 \pi \eta \, a^3 / Kt \dots\dots\dots\dots (7)$$

where, the molecule is pictured as a sphere of radius 'a', rotating in a medium of viscosity 'η', K being the Boltzman constant and T is the absolute temperature. The above equation may be rearranged as:

$$V_D = 4 \pi \eta^3 N/3 = \tau RT /3\eta \dots\dots\dots (8)$$

Where V_D is the hypothetical volume of 'N' molecules in a mole as calculated from the relaxation time and viscosity data, 'τ' is the relaxation time, 'η' is the viscosity in poise, N is the Avagadro's number (6.062 x 10^{23}), 'R' is gas constant (1.38504 x 10^{16}) and 'T' is the absolute temperature. By this method the relaxation time is determined up to an accuracy of 5%.

Results and Discussion

From the above Eq 3 to 8, the following results have been obtained.

1. From Table 1, it has been concluded that xylene isomers have higher viscosity as compared to pure naphthene and its mixture with para-xylene.

2. It has also been observed that pure naphthene has a boiling point of 149°C, which is higher than the boiling points of the three isomers which results in a higher absorption and loss.

3. Similarly, the density of xylene isomers is higher as compared to pure naphthene and its mixture.

4. The relaxation time of the molecules of ortho-xylene is 11.824 x 10^{-10}sec, while for 1:1 mixture it is about 12.56 x 10^{-10} sec., as calculated from Eq 7 and 8.

5. Viscosity and density of the above samples decrease as the temperature rises.

6. For the entire range of temperatures the dielectric constant e, increases as the temperature rises.

7. As the temperature rises the relaxation time also decreases as a general trend as observed in these liquids.

The values of complex dielectric constant $\varepsilon^* = \varepsilon' - i\varepsilon''$ and $\tan \delta$ have been determined at 303.5K which are listed in Table 2-5. For pure naphthene (Table 2) the values of real part ε' at low frequency (0.1MHz) is 2.325 and imaginary part is $\varepsilon'' = 0.981$ and $\tan \delta = 0.422$ whereas these values at high frequency of 100MHz are, $\varepsilon' = 2.494$ and ε'', 1.113 and the values of relaxation time is calculated from the Cole Cole plot of these values.

For p-xylene, the observed values of dielectric parameters (Table -3) are ε', 2.201 and ε'', 0.225 and tan δ=0.102 which are at low frequency of 0.1MHz. It is observed from this table that ε'' increases to a maximum value of 0.297 and drops at high frequencies of 30MHz to 100MHz and the data is distributed symmetrically.

For m-xylene as it is clear from Table 4, the real part of dielectric constant increases as the frequency rises, but the imaginary part (loss factor) approaches to a maximum than drops like the p-xylene.

Similar trend is observed in ortho-xylene at 303.5K and at different frequencies, as it is clear from Table 5.

As seen from Table 1, for the 1:1 mixture the calculated values of relaxation time 'τ' at four different temperatures range from 9.273×10^{-10}sec to 12.566×10^{-10}sec.

From Table 1, the value of 'τ' varies from 8.392×10^{-10} to 11.824×10^{-10} sec for pure o-xylene and these values vary from high to low temperatures. For m-xylene the value 'τ' varies from

8.972×10^{-10}sec to 9.612×10^{-10}sec. For para-xylene (99.99% pure) the value of 'τ' varies from 5.862×10^{-10}sec to 10.86×10^{-10}sec, which is the least value and is in agreement with the work of Kenith *et al* (1960) and Singh and Sharma (1993).

From the plot on the complex plane of the values of ε'' vs ε' for each of the three isomers, in Table 2-4, the Cole-Cole type of semi circles, distribution curves (Fang 1965) are obtained. Fig. 2 shows, this plot for pure ortho-xylene, the data is fitted by least square method and the values have been taken thrice at room temperature, 303.5 K. From Fig 4 the Cole-Cole type of distribution plot is obtained for the data of meta-xylene. Fig 3 is an ideal representation of Cole-Cole type of arc plot. The relaxation time obtained from Fig 1, 2 and 4 is in agreement with the cole-cole type of curve (Debye 1961).

In the above xylene isomer there is a trend of increasing value of dielectric constant ε' while the values of ε'' and tan δ becomes maximum at one high frequency value (about 40 to 70 MHz) then these values drop, giving an approximately semi circle type of distribution of data.

Table 1
Observed values of different dielectric parameters for solvents at 100KHz

Heat of vaporization* cal g^{-1}	Temp. K	Density d (g cm^{-3})	Viscosity η c poise	Apparent dielectric constant	Relaxation time $\tau \times 10^{-10}$ sec
Pure Napthene at boiling point 149°C					
89.5	305.5	0.745	0.345	2.372	6.643
	308.0	0.730	0.331	2.345	5.280
	313.0	0.722	0.322	2.401	5.912
	318.0	0.696	0.319	2.420	6.362
1:1 Mixture (napthene/p-xylene) at 167.4°C					
102.5	303.5	0.772	0.341	2.340	12.566
	308.0	0.760	0.336	2.370	11.375
	313.0	0.758	0.329	2.365	9.273
	318.0	0.689	0.313	2.612	9.752
Para xylene at boiling point 138.5°C					
81.2	303.0	0.853	0.564	2.235	10.860
	308.0	0.801	0.523	2.246	9.882
	313.0	0.843	0.489	2.251	8.765
	318.0	0.812	0.319	2.340	5.862
Ortho-xylene at boiling point 134.4°C					
83.0	303.0	0.812	0.589	2.390	11.824
	308.0	0.848	0.523	2.312	10.260
	313.0	0.864	0.495	2.261	9.107
	318.0	0.834	0.421	2.273	8.392
Meta-xylene at boiling point 131.1°C					
81.2	303.0	0.790	0.529	2.264	9.612
	308.0	0.810	0.492	2.233	9.597
	313.0	0.847	0.514	2.271	9.253
	318.0	0.819	0.414	2.281	8.972

* Heat of vaporization values available in literature (Encyclopedia of Chem. Tech., Reymond Kirk 1989).

Table 2

Dielectric parameters at different frequencies for pure naphthene at 303.5K (Room temperature)

Frequency MHz	Dielectric constant		Tan δ loss factor
	Real part ε'	Imaginary part ε''	
0.1	2.325	0.981	0.422
0.2	2.331	1.197	0.513
0.4	2.342	1.155	0.493
0.6	2.346	1.165	0.496
0.8	2.350	1.888	0.804
1.0	2.372	1.897	0.799
2.0	2.383	1.852	0.769
4.0	2.415	1.723	0.707
6.0	2.438	1.618	0.664
10.0	2.448	1.603	0.665
20.0	2.459	1.576	0.641
30.0	2.462	1.543	0.623
40.0	2.469	1.532	0.634
50.0	2.478	1.482	0.598
60.0	2.488	1.412	0.567
70.0	2.489	1.376	0.553
80.0	2.491	1.231	0.494
90.0	2.494	1.297	0.520
100.0	2.494	1.113	0.446

Table 4

Dielectric parameters at different frequencies for meta-xylene at 303.5K (Room temperature)

Frequency MHz	Dielectric constant		Tan δ loss factor
	Real part ε'	Imaginary part ε''	
0.1	2.312	0.295	0.121
0.2	2.314	0.299	0.123
0.4	2.317	0.301	0.125
0.6	2.318	0.303	0.129
0.8	2.319	0.309	0.131
1.0	2.321	0.312	0.130
2.0	2.323	0.317	0.136
4.0	2.322	0.321	0.138
6.0	2.324	0.325	0.139
10.0	2.327	0.327	0.140
20.0	2.337	0.324	0.138
30.0	2.342	0.318	0.135
40.0	2.347	0.313	0.133
50.0	2.351	0.311	0.132
60.0	2.353	0.310	0.132
70.0	2.359	0.307	0.120
80.0	2.362	0.305	0.129
90.0	2.365	0.304	0.128
100.0	2.367	0.293	0.124

Table 3

Dielectric parameters at different frequencies for para xylene at 303.5K (Room temperature)

Frequency MHz	Dielectric constant		Tan δ loss factor
	Real part ε'	Imaginary part ε''	
0.1	2.201	0.225	0.102
0.2	2.224	0.250	0.112
0.4	2.240	0.275	0.121
0.6	2.250	0.278	0.123
0.8	2.275	0.285	0.125
1.0	2.278	0.286	0.123
2.0	2.280	0.287	0.126
4.0	2.290	0.289	0.126
6.0	2.292	0.293	0.128
10.0	2.295	0.295	0.128
20.0	2.300	0.297	0.129
30.0	2.315	0.278	0.121
40.0	2.320	0.275	0.118
50.0	2.340	0.271	0.116
60.0	2.345	0.264	0.112
70.0	2.350	0.262	0.111
80.0	2.352	0.255	0.109
90.0	2.353	0.235	0.998
100.0	2.355	0.220	0.093

Table 5

Dielectric parameters at different frequencies for ortho-xylene at 303.5K (Room temperature)

| Frequency MHz	Dielectric constant		Tan δ loss factor
	Real part ε'	Imaginary part ε''	
0.1	2.289	0.074	0.0323
0.2	2.295	0.098	0.0427
0.4	2.299	0.115	0.0384
0.6	2.303	0.141	0.0612
0.8	2.319	0.161	0.0694
1.0	2.330	0.179	0.0768
2.0	2.337	0.188	0.0804
4.0	2.345	0.197	0.0843
6.0	2.351	0.193	0.0820
10.0	2.353	0.186	0.0790
20.0	2.357	0.175	0.0742
30.0	2.359	0.168	0.0712
40.0	2.362	0.155	0.0656
50.0	2.366	0.144	0.0608
60.0	2.371	0.128	0.0538
70.0	2.331	0.113	0.0476
80.0	2.377	0.102	0.0429
90.0	2.379	0.093	0.0391
100.0	2.384	0.071	0.0298
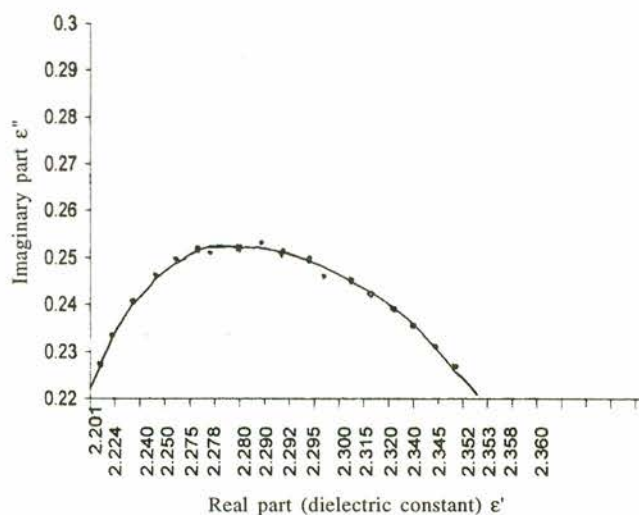
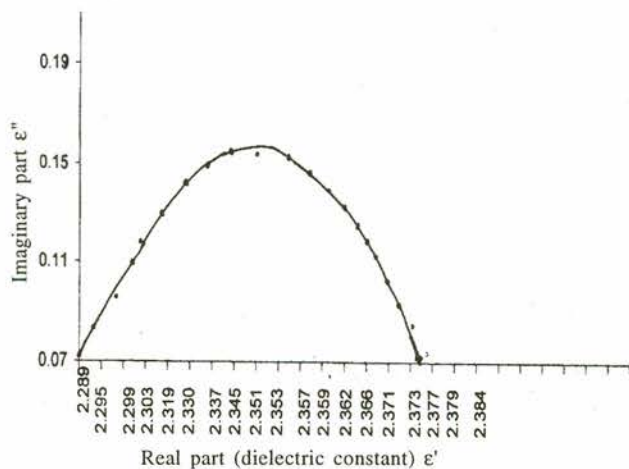**Fig 1.** Cole-Cole plot for pure para-xylene.

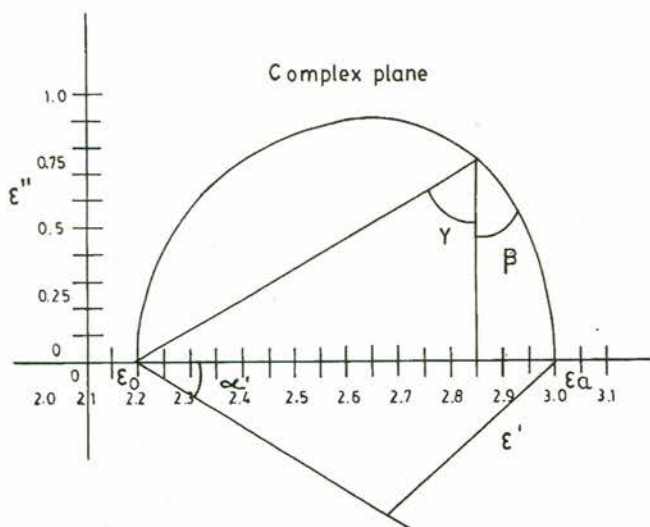**Fig 2.** Cole-Cole plot for ortho-xylene (pure).

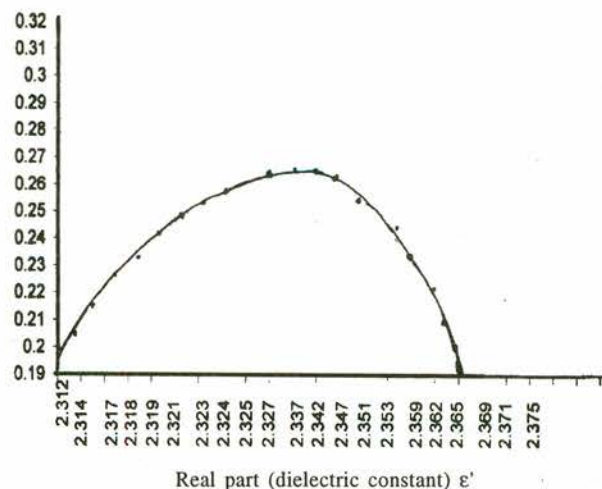**Fig 3.** Cole-Cole Arc plot (an ideal curve).

Fig 4. Cole-Cole plot for meta-xylene (pure).

The value of relaxation time at a particular frequency shows that it increases with the size of molecule and decreases with the rise of temperature. The three isomers (o, m, p) have the same molecular dimensions approximately and possess the same distribution of relaxation time or the main relaxation phenomenon is characterized by single relaxation time. But the values obtained for pure naphthene are different and higher than those of the previous three isomers which is due to the size of the molecule. In 1:1 mixture, there is also a trend of temperature dependence in decreasing the relaxation time. This solvent shows substantially higher loss at higher temperature more value of relaxation time. This loss factor is prominent in the frequency range 10 MHz to 100 MHz.

Conclusion

Dielectric constant and loss factor measurements at 0.44 to 3 cm wavelengths carried out on xylene (nonpolar) and naphthenes (polar) and mixture were examined on the basis of Cole-Cole arc plots.

The dielectric relaxation time measurements for the above liquids have been performed at temperatures starting at 303K, varying upto 318K with a difference of five degrees. Such forms of aromatic hydrocarbons have close ring structure with alternate double bonds. The three isomers have the same empirical formula weight 106.16. Relaxation time 'τ' is calculated from the Debye and Hill (eq 7 and 8). The following inferences can be drawn.

a) It has been observed that the mean relaxation time 'τ' of para, ortho, meta is found to be greater than the straight chain formula (naphthene) or mixture at these wavelengths. The presence of double bonds in this group will reduce the intermolecular modes of orientation via

various C-C bonds. Some rigidity introduced in such molecules results in a higher value of relaxation time than that expected from the molecules with similar number of carbon atoms in straight chain. Because of the existence of internal rotation it has more than one relaxation time. (Kenith *et al* 1960).

Hence this approach seems to provide better distribution function for xylene isomers. The most probable relaxation time obtained from the Cole-Cole plot is less than the respective values in pure liquid possibly due to presence of small dipolar field in solution (Alexiwicz & Wladyslaw 1994). The order of the time magnitude calculated in the naphthene molecules is larger and is comparable to the size of the molecule, which indicates a significant contribution by inter molecular process. According to Cole and Cole or Debye eq 1 and 2, when the values of ε'' at different frequencies are plotted as ordinate against the corresponding value of ε' as abscissa, on a complex plane (Fig 3), the shape of the arc of a circle is obtained. This is an ideal distribution curve. The points, at which ε' has the values ε_∞ and ε_0, are the points of intersection on the X-axis. When there is only one relaxation time, the arc is like a perfect semi circle (Fig 3) with its diameter on the abscissa. When there is a distribution of relaxation time the centre of the semi circle is depressed through an angle $\alpha' = \alpha \pi /2$, which is a measure of extent of distribution. It may be concluded, however, that the distribution of relaxation time as measured by α, (relaxation parameter) increases with increase in length of molecular chain (Price 1958).

b) The solution of non polar (xylene) solute molecules in simple polar solvents (naphthene), may have the characteristic absorption maxima, and this may increase with an increase in frequency. This can support our assumption that the overall molecular absorption in a liquid is due to their molecular rotation.

c) On the basis of the above analysis it is clear that the Debye theory represents approximately the observed molecular phenomenon and a mechanism during absoprtion. It gives the picture of a dielectric liquid which consists of spherical molecules whose rotation in an externally applied field obeys the Stoke's law. The basic quantity is the relaxation time, which is required by molecules of some dielectric material after the removal of externally applied field. The polarization of the liquid falls as compared to its initial values (Mayer and Morrison 1991).

d) As it is seen from Table 1, the dielectric relaxation time is proportional to the viscosity of solvent and their molecu-

lar weights in associated liquids and the concept of a macroscopic viscosity regarding the rotation of electric dipole is considered here by the application of the field (Jeyaraj and Sobhandri 1980).

e) If the length of the carbon-carbon chain increases in an organic molecule like long chain aliphatic alcohols (Garabadu and Swain 1993) the value of 'τ' becomes higher.

f) 'τ' also increases if the molecules of the organic solution deviate from spherical geometry (Hill 1954; Kenith *et al* 1960).

g) If the length of the carbon-carbon chain increases in an organic molecule like petroleum mixture the value of τ becomes higher.

h) In the light of the above conclusion this approach seems to provide a better distribution function for pure xylene and their naphthene mixture. As a corollary, the above results can be used to establish a criterion of recognizing a continuous distribution of relaxation time.

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