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Estimation of Molecular free length, LF, Molecular radius, Mr and Beyer's non-linearity parameter, B/A for 4O.Om and 7O.Om LC materials - A density study.

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Abstract

Thermodynamic parameters, molecular free length, molecular radius and the Bayer's non linearity parameter B/A are estimated for the first time in the case N-(p-n-butyloxy benzylidene)-p-n-alkoxy anilines, 4O.O.m and 7O.Om compounds with m= 3, to 7 and 9in the former case and m = 3, 5 to 7 and 9 in the later cases from the density data in isotropic as well as in liquid crystalline phases. All these parameters are obtained either with the temperature in an individual compound or with the spacer length or with the end alkyloxy chain number m. The results are discussed with the body of the data available on the corresponding nO.m, nO.Om and other liquid crystalline compounds. However, the molecular radius is estimated from both the density and the birefringence data and it is found that the value estimated from the birefringence data is always low compared to that obtained from density and is the case with all the LC compounds. Very interesting data is observed regarding the molecular free length between the nO.m and nO.Om compounds.

Keywords:

nO.Om liquid crystals, thermodynamic parameters, molecular radius, non linearity parameter, molecular free length.

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Introduction

In the area of soft matter physics, dilatometric studies (the density) of liquid crystal (LC) phase transitions involving different structural organizations are an intriguing topic. The density studies involving temperature variation and across different phase transformations in LC materials are well known [1–7] to provide information regarding the nature of the phase transition and the growth of the pretransitional effects. Further, such studies provide complementary and confirmatory experimental evidence for the results obtained by using other techniques, like polarizing thermal microscopy (TM) and differential scanning calorimetry (DSC), regarding the determination of phase transition temperatures, the nature of the transition, and the thermal stability of the phase of interest.

Thermal expansion coefficient, α obtained from density studies is a very important physical quantity which is used to derive different thermodynamic properties. The estimation of different thermodynamic parameters is mostly dealt in pure liquids, binary and ternary mixtures of liquids at ambient and at different temperatures [8-12]. Recent studies by Pisipati and his group [13 -17] on a number of liquid crystals and homologous series of compounds have found some interesting results regarding different thermo dynamic and related parameters. Further, it has been reported [1, 2] that the position of the electronegative oxygen in the molecular moiety plays an important role regarding the clearing temperatures, the phase variants and the manifestation of nematic phase. Our recent studies on a number of nO.m and nO.Om compounds have shown that some of the thermodynamic parameters also have shown interesting results [13 – 18]. This motivated the authors to perform the density studies on 4O.Om compounds and estimate the important thermodynamic parameters in these compounds as well as in 7O.Om compounds and compare the results with corresponding 4O.m and 7O.m compounds.

Theoretical and empirical relations

The procedure and the different expressions used for the estimation of different thermodynamic parameters are described elsewhere [19 - 22]. However, the important and the relevant expressions regarding the molecular free length, molecular radius and the acoustic Beyer's non-linearity parameter are given below for ready reference.

a) Intermolecular free length, Lf

The intermolecular free length (Lf) is given by the expression [19]

Lf = (2Va/Y) (1)

where Va is the available volume per the molecule and Y referents surface area per the LC molecule and is given by

Va = (V – V0) and Y = (36πNV02)1/3 (2)

and

V0 = (V/V~) (3)

where N is the Avogadro number, V0 and V molar volume at absolute zero and at temperature T respectively. V~ represents reduced molar volume and is given by the expression

V~ = { ((αT/3)/(1 + αT)) + 1}3 (4)

α is the thermal expansion coefficient.

b) Molecular radius, Mr

Molecular radius of the liquid crystal molecule can be obtained from density as well as from birefringence and the relevant expressions are given below.

From density [20]

$$Mr = \frac{1}{2}\ 3\sqrt{\frac{M\sqrt{2}}{\rho N}} \quad (5)$$

where M is the molecular weight of the molecule.

The Birefringence data can be utilized in conjunction with molar volume to compute the molecular radius (Mr) using the following relation [21]:

$$Mr = \left\{\left(\frac{3}{4N\pi}\right)\frac{(n^2-1)}{(n^2+2)}\ V_m\right\}1/3 \quad (6)$$

3, Beyer's non-linearity parameter

The non-linearity parameter B/A is given as [22]

B/A = 2up[du/dp]rr (7)

A general formalism for B/A in terms of the acoustical parameters for liquids and polymers has been made using the Moelwyns–Hughes parameter (C1), isobaric acoustic parameter (K) and the isothermal acoustic parameter (K"); the detailed method of calculation of K and K"from α is given elsewhere [23] obtained from the thermal expansion coefficient (α)

B/A = C1 – 1 (8)

B/A = 2(K + γK") (9)

Results and discussion

Inter molecular free length for the compounds in the 4O.Om and 7O.Om series are evaluated using the expressions from (1) to (4). The vales of Lf1 and Lf2along with values of K, K", and other values are shown for both the series in tables 1 and 2 respectively. For the sake of comparison the 4O.m and 7O.m compounds Lf1 are shown along with the values of 4O.Om and 7O.Om at TNI + 5 are shown in figures 1 and 2 respectively. From the tables it is envisaged that inter molecular fee length is slightly higher in LC phases compared to that in isotropic phase. Further, from the figures it is observed that the inter molecular free length in 4O.m and 7O.m compounds exhibits an odd even effect while it shows a linear increment with the chain length with an increment of about 0.019 Å and 0.016 Å per one chain length respectively. At this juncture this may be due to the presence of oxygen atom on both the sides of the core of the molecule. Even though the increment exhibits a decrease of about 2% with the increase of chin number on the benzaldehyde side from 3 to 7, the core molecular free length shows an increment of about 0.100 Å units.

The molecular radius, Mr estimated using the equations (5) and (6) in the case of 4O.m, 4O.Om and 7O.Om compounds are shown in figures 3 and 4 with the values of increment and core radius are given in table 3. The available volume at

TNI+5 for the compounds 4O.Om and 7O.Om compounds along with 4O.m and 7O.m compounds are drawn in figures 5 and 6. The core increment values are given in table 4. The Bayer's non linearity parameter B/A is calculated using the equations (8) and (9) for all the compounds in both the series and plotted the values at TNI+5 OC against the chain number in the figure 7 which an odd even effect as in the other liquid crystalline compounds.

The salient features observed from the study are

The molecular free length, Lf exhibits an odd-even effect in the case of 4O.m and 7O.m where as it shows an increase with chain number (Figures 1 and 2).

The molecular radius values obtained using α value are higher compared to the values obtained from birefringence, δn. (Figures 3 and 4)

In the case of available volume the homologous series 4O.Om and 7O.Om exhibit lower values compared to 4O.m and 7O.m compounds (Figures 5 and 6).

As usual the B/A values show odd even effect with the chain number (Figure 7).

References

[1] Ajeetha, N., Ramakrishna Nanchara Rao, M., Datta Prasad, P. V., & Pisipati, V. G. K. M. (2005). Z. Naturforsch., 60a, 746.
[2] Ajeetha, N., Ramakrishna Nanchara Rao, M., Datta Prasad, P. V., & Pisipati, V. G. K. M. (2006). Mol. Cryst. Liq. Cryst., 457,
[3] D. Madhavi Latha • Ch. Srinivasu • P. Pardhasaradhi • P. V. Datta Prasad V. G. K. M. Pisipati, /J. Thermal Analysis and Calorimetry, (in press) 2013.
[4] Burmistrov, V. A., Zavyaloy, A. V., Novikoy, I. V., Kuvshinova, S. A., & Aleksandriskii, V. V. (2005). Russ. J. Phys. Chem., 79, 130.
[5] Gogoi, B., Ghosh, T. K., & Alapati, P. R. (2005). Cryst. Res. Tech., 40, 709.
[6] Gogoi, B., Alapati, P. R., & Verma, A. L. (2002). Cryst. Res. Tech., 37, 1331.
[7] Datta Prasad, P. V., Ramakrishna Nanchara Rao, M., Lalitha Kumari, J., & Pisipati, V. G. K. M. (2009). Phys. Chem. Liq., 47, 123.
[8] B.K. Sharma, Pramana-J.Phys, 26, 223, (1986).
[9] B.K. Sharma, Pramana-J.Phys, 37, 489, (1991).
[10] M.S.R.Subramanyam, H.Sumathi Vedanayagam, D.Venkateshwar Rao, A.Rajaiah and Venkatacharyulu, JAOCS, 72, 1537, (1995).
[11] R.R.Reddy, A. Venkatesulu, K.Rama Gopal, K.Neelakanteswara Reddy, J.Mol.Liq,130, 112, (2007).
[12] B.K.Sharma, J.Poly.Matter, 1, 193, (1984).
[13] D.Madhavi Latah, V. G. K. M. Pisipati, K.fakrudin, M. R.N.Rao and P. V. Datta Prasad, Int. J. of Advances in Sciences and Technology, 3, 48
[14] D.Madhavi Latah, V. G. K. M. Pisipati, J. Lalitha Kumari and P. V. data Prasad, J. Mol. Liquids, 2011.
[15] D.Madhavi Latah, V. G. K. M. Pisipati, and P. V. Datta Prasad, J. Mol. Liquids, 161, 91 (2011).
[16] D.Madhavi Latah, V. G. K. M. Pisipati, and P. V. Datta Prasad, Mol. Cryst. Liq. Cryst., 144, 165 (2010).
[17] D.Madhavi Latah, V. G. K. M. Pisipati, M. R. N. Rao and P. V. Datta Prasad, Physica B, 406, 3821 92011).
[18] M. V. V. Nagi Reddy, V. G. K. M. Pisipati, D.Madhavi Latah, , and P. V. Datta Prasad, Physica B, 406, 720 (2011).
[19] J. D. Pandey and R. Dey and J. Chhabra, Phys. Chem. Comm., 6, 55 (2003).
[20] J.Pandey, D. Ranjan and B. D. Bhatt, J. Mol. Liqs., 111, 67 (2004).
[21] C. Sivaram, J. V. Rao and P. Venkatacharyulu, Cryst. Res. Tech., 25, 238 (1990).
[22] J.D. Pandey, Ranjan Dey, Vinay Sanguri, Jyotsna chhabra, T Nautiyal, Pramana, J. Phys. 65 (2005) 535..

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Captions

Table 1- Variation of thermo acoustic parameters and molecular free length in different LC phases of 4O.Om compounds
Table 2- Variation of thermo acoustic parameters and molecular free length in different LC phases of 7O.Om compounds
Table 3- The variation of values of molecular free length increment and core for 4O.m,4O.Om and 7O.m,7O.Om compounds
Table 4- The values of increment and core V0 for 4O.m, 4O.Om and 7O.m,7O.Om compounds

Figure 1-Variation of Molecular free length in 4O.m and 4O.Om compounds.
Figure 2- Variation of Molecular free length in 7O.m and 7O.Om compounds.
Figure 3-Variation of Molecular radius (Mr) in 4O.Om compounds.
Figure 4- Variation of Molecular radius (Mr) in 7O.Om compounds.
Figure 5- Variation of Available volume (Va) in 4O.m and 4O.Om compounds.
Figure 6- Variation of Available volume (Va) in 7O.m and 7O.Om compounds.
Figure 7- Variation of Bayer's non linearity parameter B/A in 4O.Om and 7O.Om compounds.

Table 1

nO.Om	Phase	Temp.	K"	K	K'	Va	V0	Lf1	V0	Lf2
4O.O3	I	117.5	0.045	4.883	4.928	53.89	265.59	0..639	258.16	0.649
	N	110	0.021	4.948	4.969	53.03	263.52	0..645	256.58	0.648
4O.O4	I	125	0.068	4.820	4.888	54.36	265.72	0.644	257.85	0.660
	N	116	0.040	4.896	4.936	53.92	266.16	0.655	258.80	0.672
4O.O5	I	116	0.109	4.711	4.819	60.79	292.98	0.752	283.41	0.695
	N	109	0.087	4.768	4.856	60.42	293.36	0.772	284.25	0.725
4O.O6	I	120.5	0.127	4.605	4.733	64.35	304.53	0.696	293.84	0.715
	N	110	0.245	4.284	4.529	66.71	302.16	0.726	288.18	0.752
4O.O7	I	108.5	0.144	4.560	4.704	67.82	319.01	0.711	307.36	0.732
	N	98.5	0.487	3.635	4.122	73.92	304.69	0.800	280.23	0.852
4O.O9	I	114	0.208	4.384	4.593	74.27	341.09	0.745	326.60	0.772
	N	104	0.694	3.113	3.807	84.85	323.06	0.883	280.33	0.971

Table 2

nO.Om	phase	Temp.	K"	K	K'	Va	V01	V02	Lf1	Lf2\
7O.O3	Iso.	111.6	0.151	4.540	4.691	64.76	303.8	292.5	0.702	0.720
	N	104.0	0.270	4.216	4.487	66.43	298.0	283.4	0.729	0.754
7O.O5	Iso.	113.1	0.220	4.352	4.572	71.48	326.8	312.5	0.738	0.760
	N	101.0	0.572	3.414	3.986	78.35	312.3	281.7	0.834	0.893
	C	95.0	0.565	3.432	3.997	77.46	309.6	279.8	0.829	0.887
7O.O6	Iso.	116.3	0.259	4.248	4.506	74.96	337.8	321.7	0.757	0.782
	N	106.1	0.600	3.344	3.943	82.11	323.8	289.9	0.853	0.918
	C	103.0	0.614	3.309	3.922	81.55	322.5	289.3	0.849	0.913
7O.O7	Iso.	114.6	0.158	4.521	4.679	76.11	356.1	342.7	0.742	0.761
	N	108.2	0.251	4.269	4.520	77.54	350.4	334.0	0.764	0.789
	C	104.0	0.537	3.504	4.041	76.90	349.4	333.6	0.759	0.783
7O.O9	Iso.	113.5	0.284	4.179	4.463	84.87	378.7	359.6	0.794	0.822
	N	106.9	0.339	4.031	4.370	85.36	373.0	351.6	0.807	0.839
	C	103.0	0.640	3.242	3.883	93.33	362.3	320.5	0.899	0.976

Table 3

Compound	Increment	Core value
4O.m	0.060	4.37
4O.Om	0.066	4.37
7O.m	0.068	4.50
7O.Om	0.064	4.57

Table 4

Compound	Increment	Core V0
4O.m	4.52	39.15
4O.Om	3.62	42.03
7O.m	3.24	54.95
7O.Om	3.17	55.33

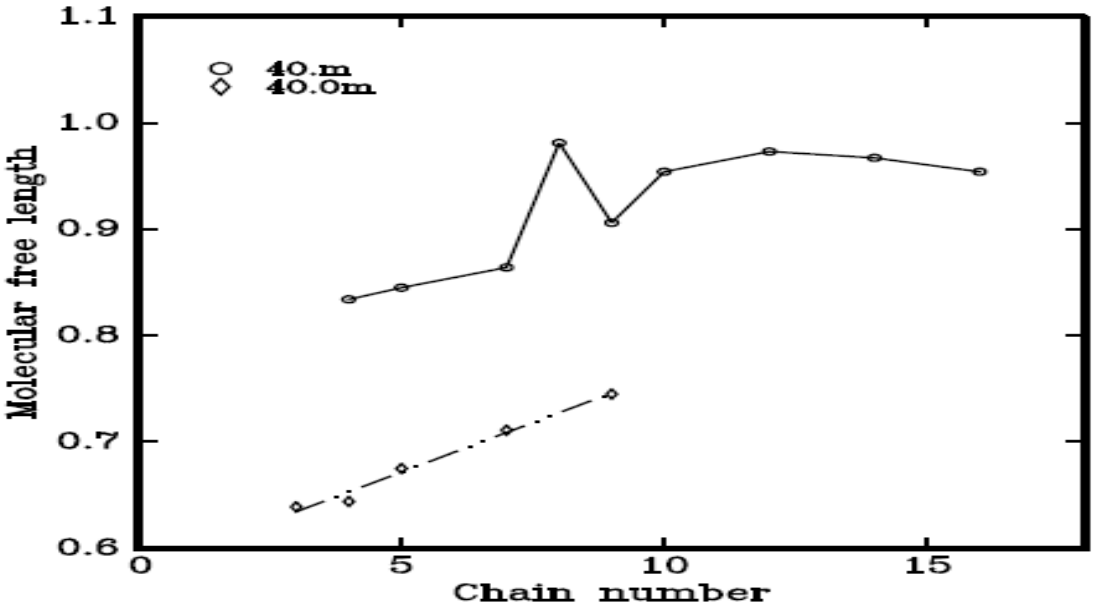


Figure 1

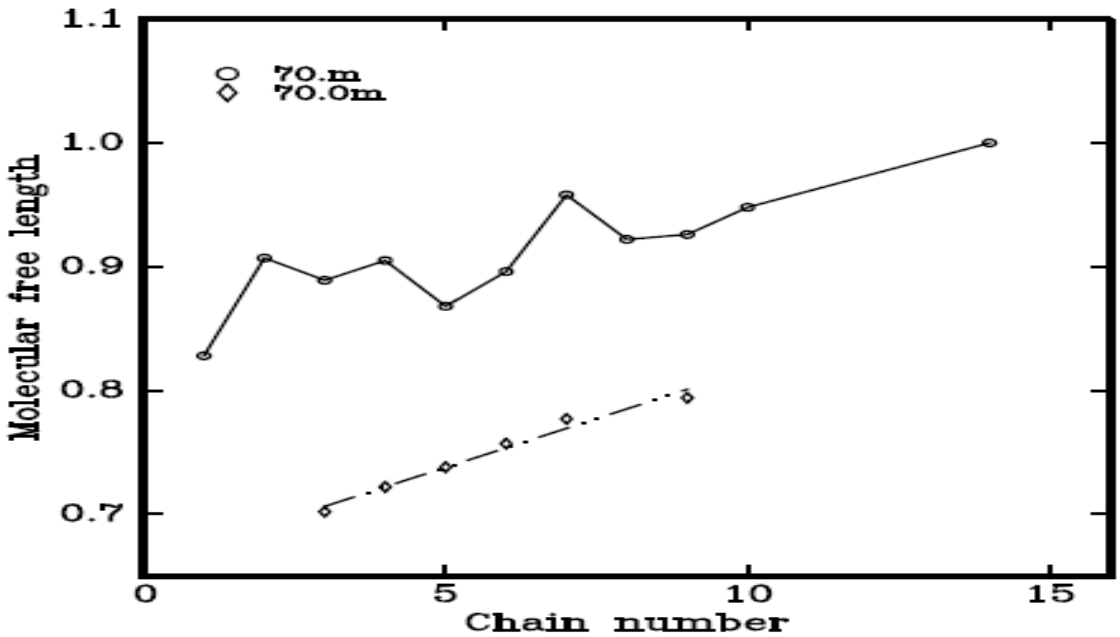


Figure 2

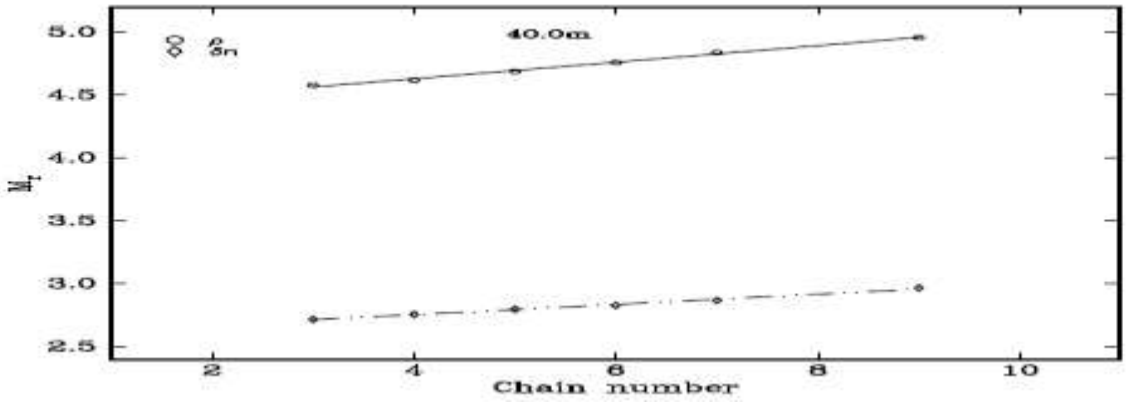


Figure 3

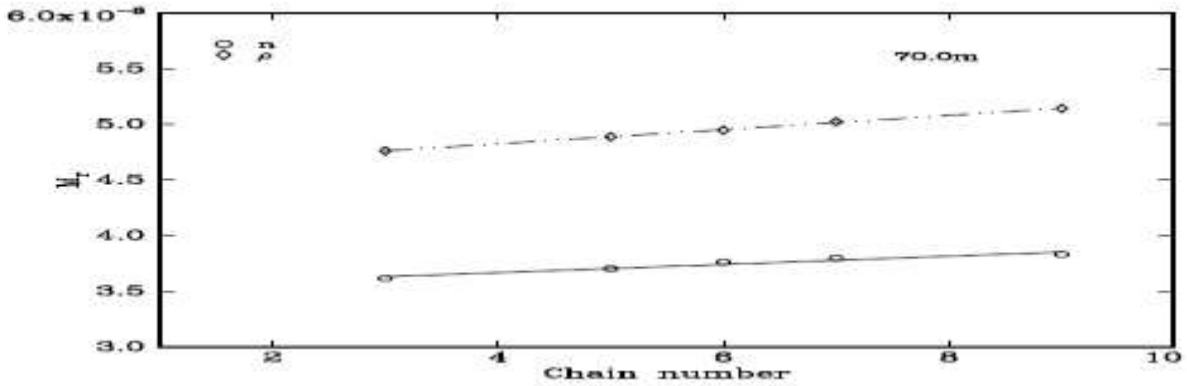


Figure 4

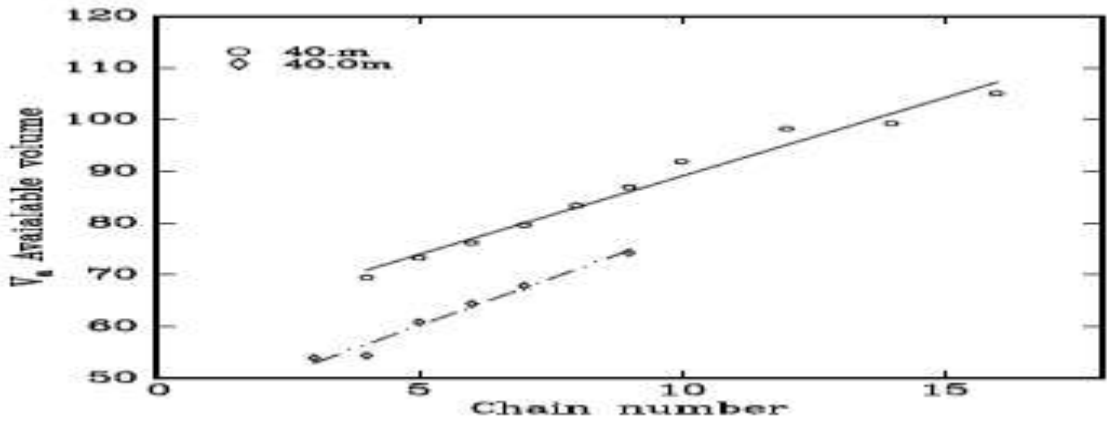


Figure 5

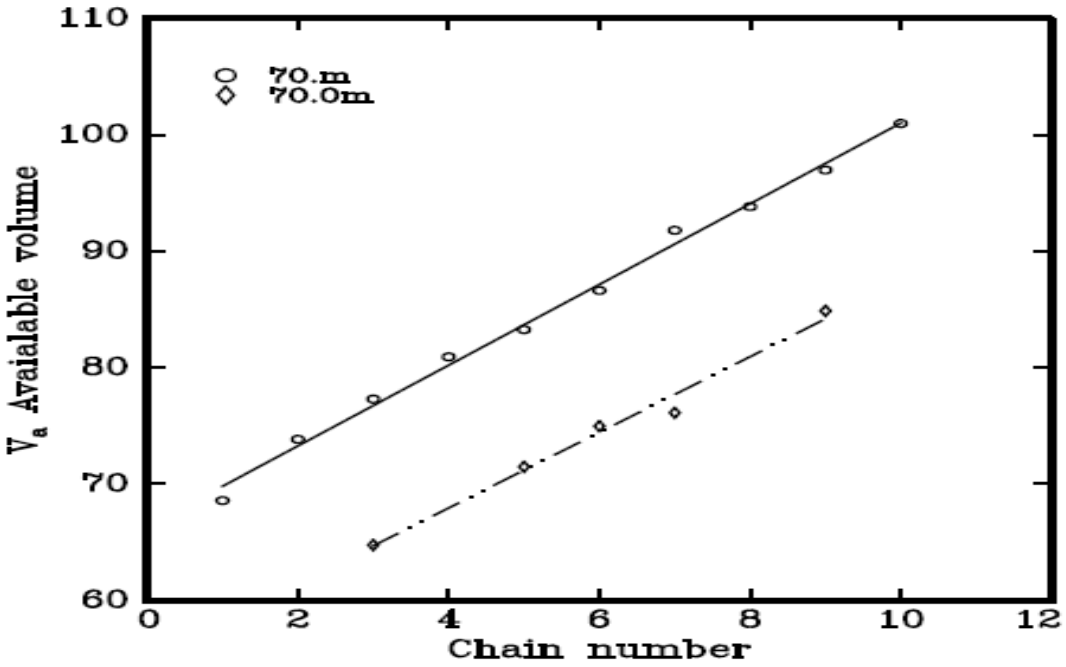
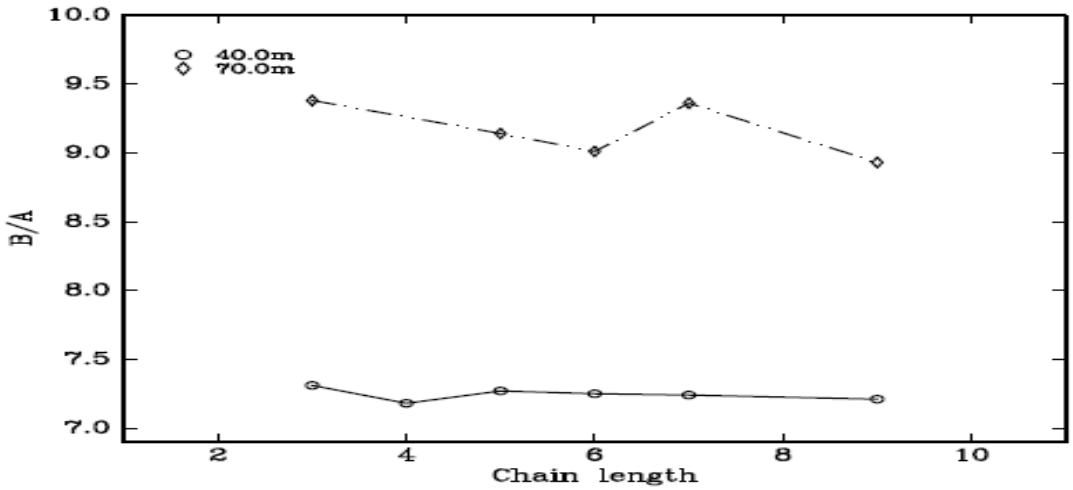


Figure 6



Figure