

DETERMINATION OF THE SOLUBILITY PARAMETERS OF A C₉⁺ CONDENSATE OIL FRACTION BY INVERSE GAS CHROMATOGRAPHY

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Received August 14, 2007, accepted November 29, 2007

ABSTRACT

The solubility parameter of a C₉⁺ condensate oil fraction, δ_2 , was determined by the technique of inverse gas chromatography (IGC). Using this oil fraction as the stationary phase, solute retention volumes were precisely determined as a function of temperature using 20 solute probes of varying solubility parameter. Solvent (oil)-solute Flory-Huggins interaction parameters, $\chi_{1,2}^\infty$, were also calculated from the solute retention data and indicate complete miscibility of the solute probes with the examined oil fraction at conditions of infinite dilution. The $\chi_{1,2}^\infty$ values and their dependence on temperature were used to compute δ_2 at 100, 90 and 80 °C. Over this temperature interval, δ_2 , decreases from 10.1695 to 9.6322 (cal./cm³)^{1/2} with increasing temperature, a trend consistent with the loss of cohesive energy density in the liquid condensate oil.

Keywords: Inverse Gas Chromatography, Solubility Parameter, Condensate Oil, Flory-Huggins interaction Parameter

1. Introduction

The regular solution theory, or solubility parameter theory as developed by Hildebrand [1,2] has been used in many areas of technology [3] to explain various aspects of solution and solubility behavior. The key factors in this theory are the solubility parameters, which are defined as the square root of the cohesive energy densities of the solute and solvent, respectively. A basic tenet of the above theory the maximum solubility of the given solute-solvent system is attained when the solute and solvent cohesive energy densities, i.e. the measure of cohesions within the liquids, are identical. The cohesive energy density may be estimated using Hildebrand's solubility parameter calculated either from the vaporization energy or from the surface tension:

$$\delta = (\Delta E/V)^{1/2}$$

Where ΔE denotes cohesive energy and V is the molar volume of the solute. This simple method allows a satisfactory solubility prediction of a large range of solutes in non-polar solvents.

Solubility parameters of non-volatile materials, such as polymers have traditionally been difficult to determine by direct experimental measurements but have been inferred from the solubility measurements of these macromolecules in a variety of the solvents having known solubility parameters [4] or from a group contribution scheme based on molecular structure correlations [5,6]. The development of inverse phase gas chromatography can be used for measurement of the solubility parameter of a non-volatile material from the solubility parameters of different solutes in the solvent (stationary liquid).

Information on the solubility of light gases in hydrocarbons and their mixtures is important for: (i) processes related to petroleum production and refining. Recently Riazi and Vera [7] showed that the Scatchard-Hildebrand solubility model can be used to calculate the solubility of gases in petroleum fractions through their paraffin, naphthene and aromatic (PNA) composition. The model can also be used to predict the most suitable solvents for the wax precipitates, which buildup during the transported of these waxy oils through pipelines from petroleum field to refinery [8] and flocculation behavior of this waxy material at lower temperatures. Although, the condensate oils are considered to become more important in the future of the petroleum industry but most of the published studies are on crude

oils. In this study the solubility parameters of the condensate oil C₉+ fraction at 100, 90 and 80°C were calculated by inverse gas chromatography in a column packed with the condensate as the stationary phase using the current modal based on the Flory-Huggins theory^[9-11].

2. Experimental

The examined condensate oil was a sample from the Karanis-1x field of the Khalda Co., Egypt. The original condensate oil is analysed by gas chromatography on a PONA 100 m x 0.25 mm x 0.25 µm capillary column for determination of its total composition from C₂-C₃₆⁺.

A Claurs-500 Perkin-Elmer gas chromatograph with FID was used to evaluate the condensate oil C₉ fraction as stationary phases in packed columns. The condensate was prepared as stationary phase in the usual way by dissolving the requisite amount in petroleum ether (b. p. 60-80°C) mixed with 5 g of Chromosorb-W (80-100 mesh size) then evaporating of the petroleum ether to give a 10 % coated support was obtained. This coated support was placed in an oven at 125°C (boiling point of n-octane =125-127°C) for 1 hours for conditioning and evaporation of the C₂-C₈ fraction. This conditioned coated support was packed into a 1/8" x 6.5' stainless steel column. Another sample of the condensate oil was subjected for the same heating procedure without coating onto a solid support and analyzed by GC on a PONA column for determination composition changes. The same sample was also analysed on a 30 m x 0.25 I.D. x 0.25 µm of 100% dimethylpolysiloxane stationary phase according to ASTM D5442 and IP 372/85 for determination the % of n-alkanes and non-alkanes.

The following compounds were used as test solutes: dispersive solutes C₅-C₉ n-alkanes; polar solutes: benzene (polarizable), 1-hexene, toluene, ethylbenzene, methylenechloride, 2-butanone, 4-methyl-2-pentanone and diethylether and hydrogen bonding solutes: 2-propanol, 1-butanol, pyridine, thiophene, trichloromethane and carbontetrachloride. These test solutes were injected individually under the following GC conditions: oven temperature 80-100 °C, injector and detector temperatures 200 and 250°C. helium flow rate 16.5 ml/min (5psi) sample size 1 µL.

All the chemicals used were purchased from Aldrich and Sigma companies. Chromosorb-W and stainless steel columns were purchased from Supelco Company. Capillary columns were purchased from Thames Restek UK, Ltd.

3. Calculations

In inverse gas chromatography the investigated material (stationary phase) is placed into the chromatographic column. The volatile compounds (test solutes) are injected into the column and transport over the examined material by the carrier gas. Each test solute interacts with investigated material. The magnitude of this interaction is reflected in the value of specific retention volume^[12] (V_g) and is further presented as the Florry-Huggins interaction Parameter ($\chi_{1,2}^{\infty}$).

This method has been applied for characterization a wide range of materials, e.g. polymers^[13-15], surfactants^[16,17], pharmaceutical powdered and pharmaceutical products and porous solids^[18]. The relationship between chromatographic and thermodynamic parameters is given in the term of Florry-Huggins interaction parameter^[19].

$$\chi_{1,2}^{\infty} = \ln (273.15R / p_1^{\circ} V_g M_1) - p_1^{\circ} / RT. (B_{11} - V_1^{\circ}) + \ln (\rho_1/\rho_2) - (1-V_1^{\circ}/V_2^{\circ}) \quad [1]$$

Where 1 denotes the solute, 2 denotes the examined material, M₁ is the molecular weight of the solute [g/mole], T is the temperature of the experiment, p₁^o is the saturate vapor pressure of the solute [Pa]^[21], B₁₁ is the second virial coefficient of the solute [cm³/mole]^[21], V₁^o is the molar volume [cm³/mole], ρ₁ is the density [g/cm²] and R is the gas constant [J/mole.K].

Mass activity coefficient, Ω₁[∞] is given by:

$$\Omega_1^{\infty} = \ln (a_1/w_1) = \ln (273.15R / p_1^{\circ} V_g M_1) - p_1^{\circ} / RT. (B_{11} - V_1^{\circ}) \quad [2]$$

Where a₁ is the activity coefficient and w₁ is the mass of the solute.

Guillet and co-works^[22,23] proposed the estimation of the solubility parameter of a polymer by the following equation:

$$\bar{\delta}_{1i}^2 / RT - \chi_{(1,2)i}^{\infty} / V_1^{\circ} = (2\bar{\delta}_2 / RT) \cdot \bar{\delta}_{1i} - \bar{\delta}_2^2 / RT \quad [3]$$

If the left hand side of equation [5] is plotted against $\bar{\delta}_{1i}$, a straight line having a slope of 2 $\bar{\delta}_2$ /RT and an intercept of - $\bar{\delta}_2^2$ /RT is obtained. The solubility parameter can be calculated from the slope or the intercept of the straight line.

4. RESULTS AND DISCUSSIONS

The composition of the original condensate oil according to gas chromatographic analysis was as follows: 70.53 % C₂-C₁₆ and 29.47 % C₁₇-C₃₆⁺. The C₁₇-C₃₆⁺ fraction contains about 7.968 % n-alkane and 21 % non-n-alkanes. The examined fraction ranged from C₉-C₅₁ with a minimal number of C₉ isomers. The lighter fraction C₂-C₈ represents ca. 41.646 % of the original condensate. The carbon number distributions of the original condensate oil and its derived C₉₊ fraction are shown in Figs. 1 and 2. Some physical characteristics data required for the later calculations were derived from the GC analysis of the C₉⁺ fraction: average molecular weight = 176.0483; C₉⁺ density equal 0.801173 g/cc. Fig. 3 shows a chromatogram for n-C₆ to n-C₉ test solutes on the examined condensate oil stationary phase. It can be observed that the straight base line indicating that the condensate oil has no significant bleed at the column temperature used. Accordingly, the retention times of the test solutes remain constants after several runs.

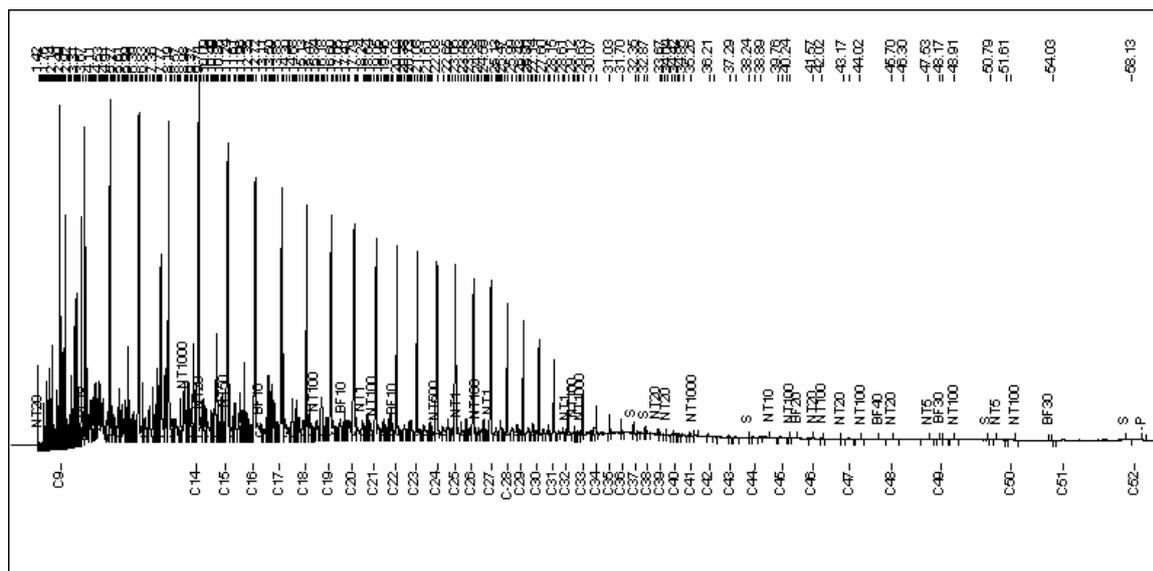


Fig. 1: The chromatogram of the examined C₉-C₅₂ condensate heavy fraction on 30 m x 0.25 μm x 0.25 film thickness capillary column.

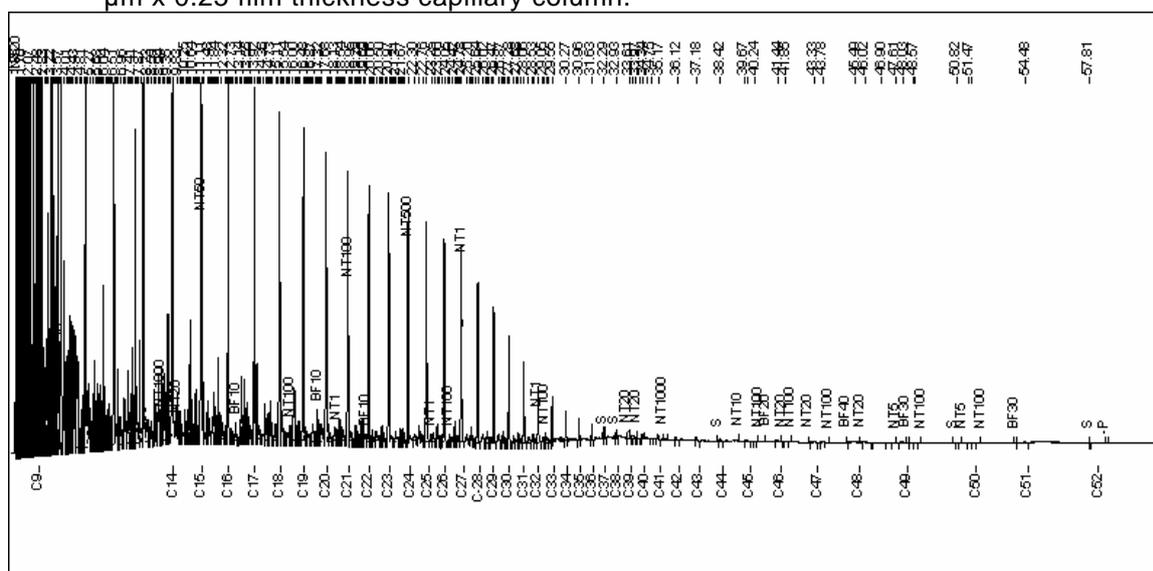


Fig. 2: The chromatogram of the original condensate oil on 30 m x 0.25 μm x 0.25 film thickness capillary column.

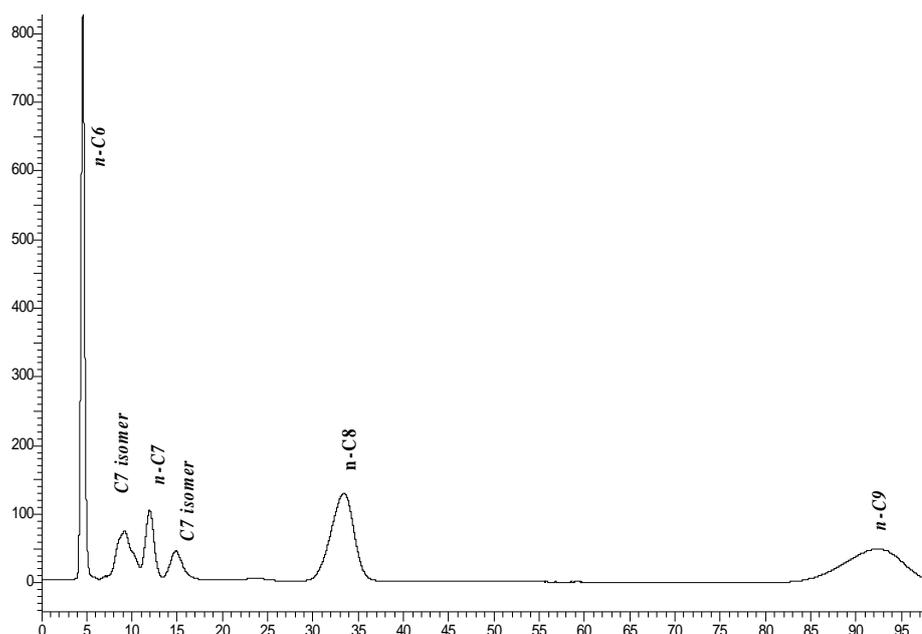


Fig. 3: The chromatogram of n-C₆ to n-C₉ test solutes on the condensate oil stationary phase at 90°C.

The resultant V_g° data are shown in Table 1 as a function of temperature for dispersive, hydrogen bonding and polar solute. The trends in V_g° with temperature are similar to those found in many other thermodynamic gas chromatographic studies [23] namely, there was a decrease in retention volume with increasing column temperature. Likewise, within a solute class, the retention volume increases with solute carbon number in a homologous series at a given temperature. Table 2 lists the derived weight fraction activity coefficients computed from Equation 4. There are several interesting trends in the data contained in Table 2 within each class of solutes, between classes of solutes, and as a function of temperature. For example, n-octane and n-nonane exhibit a decreasing escaping tendency (lower $\Omega_{1,2}^\infty$) from solution as the temperature is decreased. A similar trend is also noted for the polar and hydrogen bonding solutes used in this study, except for 2-butanone, 2-propanol and pyridine. However, inspection of the values of $\Omega_{1,2}^\infty$ for the dispersive, polar and hydrogen bonding solutes reveals a distinct dependence on the solution temperature. Weight fraction activity coefficients appear to be lowered for ethylbenzene when compared to values exhibited by other solute classes at the same temperature. This gives an indication about the greater solvation effect and the nature of the aromatic content of the examined oil. However, a high escaping tendency is exhibited comparatively by normal alcohols and ketones, while the aromatics and n-alkanes seem to prefer partitioning into the examined oil matrix. Also, the lower escaping tendency of pyridine and thiophene gives an indication about the hetero-atoms content of the examined oil.

The weight fraction activity coefficient data in Table 2 suggests that there are both subtle and regular trends in the $\Omega_{1,2}^\infty$ values as a function of molecular structure within classes of solutes. For example, the n-alkane data indicate that higher molecular weight homologues have higher $\Omega_{1,2}^\infty$ at all temperatures studied, with the exception of an inversion in this trend between n-hexane and n-heptane. Conversely, addition of methylene groups to a branched chain of the aromatics resulting in a decrease of $\Omega_{1,2}^\infty$ for the higher homologues. This suggests that methylene-methylene interactions between the similar molecules of the examined oil and the solutes are crucial to enhancing solubility of the solute in the oil phase.

The Flory–Huggins interaction parameter $\chi_{1,2}^\infty$ is a measure of the free energy of the interaction between the probe and the examined material (oil or oil mixture). The values of $\chi_{1,2}^\infty$ parameters for the set of the selected test solutes computed from Eq. 3 is presented in Table 3. Very low values of $\chi_{1,2}^\infty$ ($\chi_{1,2}^\infty < 0$) indicate strong intermolecular interactions between the solute and the liquid stationary phase while high, positive values characterize systems with weak interactions. Therefore, we may conclude that all the selected probes interact with the examined C₉ condensed oil fraction. High negative values of $\chi_{1,2}^\infty$ are found, in all cases, for the n-alkane probes, for aromatic hydrocarbons and for oxygenates on the oil stationary phase. This could lead to the conclusion that the examined oil would probably exhibit complete mutual miscibility with probes of different polarities. It means that the investigated oil exhibits multi-interaction characters. Values of $\chi_{1,2}^\infty$, most often

decrease with increasing temperature of IGC experiment. The aromatics exhibit a slightly greater mutual solubility than n-alkanes and oxygenates.

Table. 1 Values of specific retention volume (V_g°) for the selected probes on the examined condensate oil

Component	V_g°		
	100 °C	90 °C	80 °C
n-pentane	193.590	212.949	232.308
n-Hexane	314.391	323.296	406.152
n-Heptane	920.716	929.234	972.598
n-Octane	1537.881	1741.926	2339.345
n-Nonane	3325.886	3946.532	4876.927
1-Hexene	374.791	326.780	399.958
Benzene	483.976	518.822	638.848
Toluene	1130.180	1285.440	1648.228
Ethylbenzene	2185.247	2303.725	3565.546
Dichloromethane	132.803	135.900	163.777
3-Methyl-2-pentanone	773.200	858.767	1190.193
2-Butanone	125.447	111.895	171.908
Diethylether	25.554	32.136	58.077
1-Butanol	773.200	858.767	1190.193
2-Methyl-1-propanol	449.130	468.489	718.607
2-Propanol	198.236	193.977	295.806
Pyridine	1374.878	1374.878	1723.728
Thiophene	554.443	580.771	619.876
Trichloromethane	132.803	135.904	163.777
Carbontetrachloride	132.803	135.900	163.777

Table 2 Values of mass activity coefficient ($\Omega_{1,2}^\infty$) for the selected probes on the examined condensate oil.

Component	$\Omega_{1,2}^\infty$		
	100°C	90°C	80°C
n-Pentane	0.01495	0.01200	0.00982
n-Hexane	0.00617	0.00578	0.00342
n-Heptane	0.00113	0.00111	0.00100
n-Octane	0.00109	0.00082	0.00041
n-Nonane	0.00069	0.00046	0.00029
1-Hexene	0.00721	0.00989	0.00621
Benzene	0.00493	0.00420	0.00260
Toluene	0.00132	0.00098	0.00055
Ethylbenzene	0.00024	0.00021	0.00008
Dichloromethane	0.02644	0.02507	0.01631
3-Methyl-2-pentanone	0.00135	0.00106	0.00050
2-Butanone	0.12695	0.16517	0.06145
Diethylether	2.58095	1.52263	0.38976
1-Butanol	0.00373	0.00293	0.00138
2-Methyl-1-propanol	0.00576	0.00523	0.00195
2-Propanol	0.03033	0.03189	0.01207
Pyridine	0.00075	0.00075	0.00046
Thiophene	0.00237	0.00213	0.00184
Trichloromethane	0.02376	0.02253	0.01466
Carbontetrachloride	0.02104	0.01995	0.01298

From heavy petroleum fraction composition point of view ^[24], the following observations can be made: (i) the highly negative value of $\chi_{1,2}^\infty$ for ethylbenzene gives an indication about the degree of solubilization caused by condensed naphthenic and aromatic structures; (ii) for thiophene this is due to the presence of major sulphur species in heavy fractions as the thiophenics; (iii) for 1-butanol it indicates the presence of concentrated oxygenated aliphatic or naphthenic structures and (iv) for pyridine and thiophene it gives an indication about the inclusion of hetero-atoms in condensed naphthenic and aromatic structures. These solubility results give indications about a model

of condensed naphthenic aromatic structures containing inclusion hetero-atoms in its skeleton [24]. The miscibility of these oil components changes with temperature and there is a region of potential limited miscibility. The start of this region is observed at room temperature. The most suitable diluent solvents for these heavy petroleum fractions should have similar solubility characteristics. [8]

Table 3 Values of Flory–Huggins parameter (χ_{12}^{∞}) for the selected test probes on the examined condensate oil.

Component	χ_{12}^{∞}		
	100°C	90°C	80°C
n-Pentane	-2.8917	-2.9870	-3.0740
n-Hexane	-3.1717	-3.1996	-3.4278
n-Heptane	-3.7985	-3.8077	-3.8533
n-Octane	-3.7176	-3.8422	-4.1370
n-Nonane	-3.8221	-3.9932	-4.2049
1-Hexene	-3.1095	-2.9724	-3.1745
Benzene	-3.1760	-3.2455	-3.45361
Toluene	-3.8483	-3.9770	-4.22562
Ethylbenzene	-4.4752	-4.5280	-4.96476
Dichloromethane	-2.1453	-2.1684	-2.35495
3-Methyl-2-pentanone	-3.7402	-3.8452	-4.1715
2-Butanone	-1.8463	-1.7319	-2.1613
Diethylether	-0.7800	-1.0092	-1.6010
1-Butanol	-3.3622	-3.4671	-3.7935
2-Methyl-1-propanol	-3.1736	-3.2158	-3.6436
2-Propanol	-2.5532	-2.5315	-2.9535
Pyridine	-3.9173	-3.9173	-4.1435
Thiophene	-3.3509	-3.3973	-3.4625
Trichloromethane	-2.0006	-2.0236	-2.2102
Carbontetrachloride	-1.9122	-1.9352	-2.1218

The values of total solubility parameter at different temperatures for the examined oil were computed from Eqs. (5), as shown in Fig. 4, using the retention data of twenty probes of different polarities are given in Tables 4. The δ_t value of the stationary phase calculated from the slope is different from that calculated from the intercept of the straight line. This indicating that the solubility parameter of the examined oil depends on the probe polarity. The same relation trend is observed with C_9^+ crude oil fraction stationary phases with lower asphaltene concentrations [25] i.e. the activity of the condensed aromatic and naphthenic structures with respect to polar probes increases with decreasing concentrations in the examined petroleum fluid.

Table 4 Variation in solubility parameter, $(\text{cal./cm}^3)^{1/2}$, of the examined condensate oil with temperature.

Temp., C	slop	intercept	δ_t from slop	δ_t from intercept	δ_t	r
100	0.0139	-0.113	10.3158	8.9485	9.6322	0.9794
90	0.0142	-0.1161	10.5384	8.8933	9.7159	0.9792
80	0.0149	-0.1202	11.1099	9.2291	10.1695	0.9825

Table 5 Comparison between solubility parameter, $(\text{cal./cm}^3)^{1/2}$, of the examined condensate oil fraction at 80°C with some reported results.

C_9 heavy petrol. fraction	δ_t	another ^c method	annotation
The examined C_9 fraction ^a	10.1695	---	^a The average solubility parameter value of the examined oil at 353 K.
C_9 crude oil fraction-1 ^d	7.78	8.12	^b the asphaltene content: fraction-1 = 21 %; fraction-2 = 5; fraction-3 = 0.6 % and fraction-4 partly deasphalted. The solubility parameter was determined at 323 K.
C_9 crude oil fraction-2	8.085	8.19	
C_9 crude oil fraction-3	10.03	10.37	^c the solubility parameter value calculated from the onset of asphaltene flocculation data measured at 298 K ⁽²⁴⁾ .
C_9 crude oil fraction-4	9.845	---	

The calculated δ_t value for the examined C_9^+ condensate fraction is compared with other reported solubility parameters for crude oil fractions with different asphaltene concentrations to show the location and the difference between the solubility of the condensate heavy fraction and crude oil

fractions, (Table 5). It can be observed that the calculated δ_t value for the examined condensate oil fraction is greater than that of crude oil fraction-3, that has 0.6 % asphaltene content. Also, the calculated δ_t value from the intercept at 80°C is equal to that reported for the partly deasphalted crude oil fraction- 4. This give an indication about the more active concentration of the condensate naphthenic and aromatic structures in the examined sample, which is an agreement with the results, obtained by Mutelet et al [25] on solubility study of C9+ crude oil fractions. The examined condensed oil fraction is characterized by high solubility parameters and so it is rather unstable.

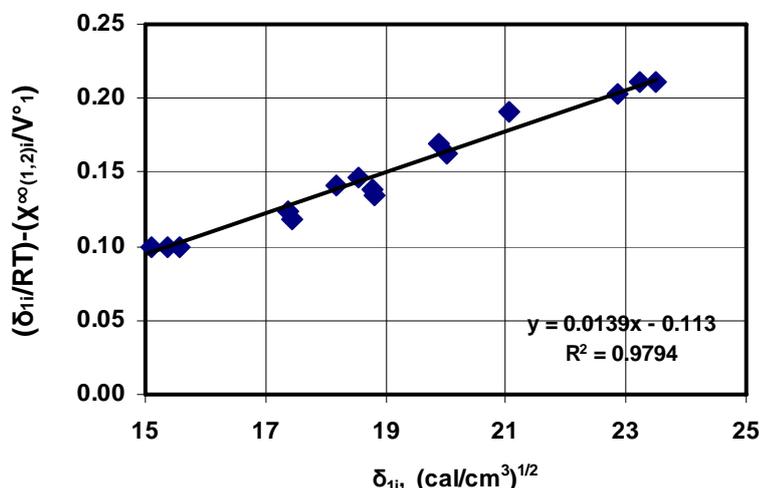


Fig. 4: Determination of the total solubility parameter δ_t at 100 °C according to Eq. [3].

5. Conclusions

Mass activity coefficient, $\Omega_{1,2}^{\infty}$, Flory-Huggins interaction parameter, $\chi_{1,2}^{\infty}$ and solubility parameter, δ_t and its components were calculated from inverse gas chromatographic data. The solubility parameter results were compared with the published results. The obtained results reveal that the probed condensed naphthenic aromatic structures are present in active concentration, which causes the high solubility and instability of the condensate oil fraction.

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