

## Assessment of oil polarity: Comparison of evaluation methods

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Received 15 May 2007; accepted 11 July 2007

Available online 25 July 2007

### Abstract

In multiple emulsion systems, oily or aqueous transfers may occur between the dispersed droplets through the continuous phase. These transfers are controlled by both the surfactant system (micellar transport), and the partial solubility of one phase in another (molecular transport). The latter could be anticipated from the knowledge of oil polarity, if this information could easily be obtained. In this work, the relative polarity of eight oils used for various purposes has been evaluated from the comparison of their dielectric requirement for solubilization, their interfacial tension and chromatographic analysis. The results showed the complementarities of HPLC analysis and interfacial tension measurements and their superiority over the solubilization method for classifying oils as a function of their polarity.

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**Keywords:** Multiple emulsions; Molecular transport; Oil polarity; Interfacial tension; HPLC

### 1. Introduction

The knowledge of oil polarity is often necessary in colloidal science. Indeed, it has a particular relevance in the understanding and the control of the formulation and stability of preparations in which water and oil coexist, such as dispersed systems (simple emulsions, multiple emulsions, gels, liposomes ...) (Chanamai et al., 2002; Capek, 2004). In the case of water-in-oil (or oil-in-water) emulsions, it is well known that aqueous (or oily) mass transfers are likely to occur between the dispersed drops, through the oily (or aqueous) continuous phase. This behavior, which is known as the ripening phenomenon, can be induced by a difference in either the drops size (Ostwald ripening) or concentration (composition ripening) (McClements et al., 1992; Taylor, 1998; Avendano Gomez et al., 2000). Aqueous or oily transports through the oily or aqueous membrane of multiple emulsions are also observed, resulting in swelling or shrinking of the multiple drops (Jager-

Lezer et al., 1997; Stambouli et al., 2007). These transfers are probably highly influenced by surfactants, which are necessarily present in these emulsions, and that give sometimes direct or reverse micelles, inside which the aqueous or oily transport will be made easier. However, some authors have suggested that micellar transport was not always the main mechanism and that the transfer could also be due to molecular diffusion. This second mechanism seems to be supported by both various experimental observations and theoretical considerations (Kabalnov et al., 1990; Kabalnov, 1994). In that case, it is obvious that oil polarity is a very important and even crucial parameter to determine in order to anticipate and control this transport.

Several characterization methods of oil polarity have been proposed in the past. However, very few have been assessed by a systematic and comparative scientific study. A method that is often mentioned consists in measuring the dielectric constant of oil (Carey and Hayzen, 2001). Although it is used in the oil industry to check the quality of oils, detect an alteration due to the presence of contaminants, it is seldom used to actually determine the polarity of oil or its solubility in water. Another test, which was derived from the previous one and frequently used in pharmaceuticals to determine the solubility of a

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drug in a solvent, consists in dissolving the studied compound in dioxane–water mixtures of known dielectric constants with increasing water contents. This method allows determination of the dielectric requirement for drug solubilization (Critchfield et al., 1953; Moore, 1958; Paruta et al., 1962; Lordi et al., 1964). Chromatographic techniques and surface tension measurements are also among the methods proposed to evaluate oil polarity.

The aim of this work was to evaluate and compare the polarity of eight different oils used for various purposes (emulsification, solubilization, lubrication . . .), by using three approaches: the assessment of their solubility in water-dioxane mixtures, a chromatographic analysis and interfacial tension measurements. A comparison of the results obtained by these three tests allowed drawing their advantages and limitations.

## 2. Materials

Liquid paraffin (PLL) was provided by Cooper (France). The two naphthenic oils (T9 and T22) were purchased from Nynas (France), isopropyl palmitate (IPP) and caprylic/capric triglyceride (GTCC) were obtained from Croda (France). *n*-Hexadecane (HDC) and 1-decanol (DC) were provided by Sigma (France) and ethyl-2 hexyl pelargonate (PEH) by Stearinerie Dubois (France). 1,4-Dioxane was purchased from VWR (France). The ultrapure water was produced by a Synergy 185 Millipore apparatus coupled with a RiOs<sup>TM</sup>5, with a resistivity of 18.2 M $\Omega$ /cm. HPLC Grade methanol and chloroform used as the HPLC mobile phase were provided by VWR (France).

## 3. Methods

### 3.1. Evaluation of oil solubility by the solubilization method

The maximum solubility of the eight investigated oils was determined in water ( $\epsilon = 78.5$ )–dioxane ( $\epsilon = 2.2$ ) mixtures with increasing dielectric constants (from 2.2 to 38). Each experiment was performed twice at 23 °C. Successive aliquots of oil were added to the water–dioxane mixtures until the solution became cloudy. The mixtures were stirred between each addition using a magnetic stirrer. After the first addition of oil resulting in a phase separation the mixtures were allowed to rest at equilibrium during 10 h in order to verify that the maximum solubility had been reached.

### 3.2. Interfacial tension measurements

Oil/water interfacial tensions ( $\gamma$ ) were measured using an automatic thermostated digital tensiometer (Krüss K10T, Hamburg, Germany) as previously described (Ringard-Lefebvre et al., 2002). The Wilhelmy plate caught at the air/water interface was progressively and carefully covered with oil, and the interfacial tension was continuously recorded for 20 h at 23 °C. The reported surface tension values are mean values of at least two measurements. The experimental uncertainty was estimated to be 0.2 mN/m.

### 3.3. High-performance liquid chromatography

The classification of oils by HPLC was based on their partition between a non-polar stationary phase (C18) and the mobile phase using a linear gradient from methanol to chloroform. The HPLC consisted of a TSP P1000XR pump and SCM1000 vacuum degasser (Thermo Separation Products, CA, USA), a 10  $\mu$ L manual injector (Rheodyne Rohnert Park, CA, USA), a Croco-CIL column oven (CIL, Sainte Foy la Grande, France), an evaporative light scattering detector (ELSD), DDL11 Cuno (Eurosep, Cergy, France) and a KromaSystem 2000 1.6 software (Bio-Tek Kontron Instruments, Milan, Italy) for data acquisition and processing. The nebulisation pressure was set to 1 bar (air), and the drift tube temperature to 40 °C. The column was a Kromasil C18 (250  $\times$  4.6 mm), (5  $\mu$ m) (Interchim, Montluçon, France), thermostated at 35 °C. A linear gradient from 100% methanol to 100% chloroform in 20 min was used. The elution rate was 1 mL/min. Detection was performed by the ELSD system. From its principle of operation ELSD is able to detect any solute less volatile than the mobile phase. Prior to their injection into the column, six of the studied oils were dissolved in the pure solvents or in their mixtures (Table 1), and the solutions were vortexed for 1 min. Decanol and hexadecane were directly injected into the column without previous solubilization in the solvents because the signal was too low when they were diluted. All analyses were performed twice.

## 4. Results

### 4.1. Determination of oil solubility by the solubilization method

The comparison between oils was estimated from the weight of oil, which could be solubilized in a dioxane–water mixture

Table 1  
Protocol of preparation of the studied samples

	Isopropyl palmitate (IPP)	Liquid paraffin (PLL)	Naphtenic oil T22	Naphtenic oil T9	Caprylic-capric triglyceride (GTCC)	Ethyl-2 hexyl pelargonate (PEH)
Oils ( $\mu$ L)	20	20	20	60	20	20
Methanol (mL)	20	20	20	20	20	20
Methanol–chloroform (2:1, v/v) (mL)	0	20	20	20	0	0

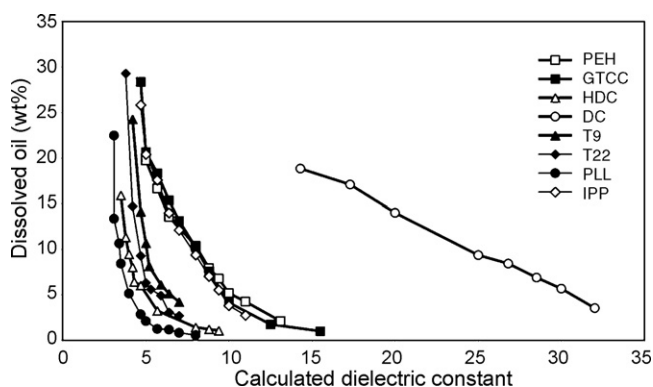


Fig. 1. Mean weight percentages of oil dissolved into dioxane–water mixtures versus the dielectric constant of solvent mixtures as calculated from the data in Critchfield et al. (1953).

of calculated  $\epsilon$ . Although the maximum solubility could not be accurately determined due to the apparently high solubility of some of the studied oils, this method allowed the comparison of oils at a given dissolved weight percentage. The results plotted in Fig. 1 are mean values of the percentages of oil dissolved in the solvent mixtures as a function of the dielectric constant of these mixtures, deduced from the data published by Critchfield et al. (1953). Deviations from the mean values were lower than 0.4 wt% for PLL, PEH, IPP and GTCC, and ranged between 1.0 and 1.9 wt% for T9, DC, HDC and T22.

The higher the dielectric requirement for oil solubilization is, the higher its apparent polarity. The comparison of the plots in Fig. 1 shows three groups of oils: PLL, HDC, T22 and T9 appear as the less polar oils, whereas DC exhibits, by far, the highest polarity. IPP, PEH and GTCC seem to have the same intermediate dielectric requirement for their solubilization. If one considers the dielectric constant necessary to allow dissolution of about 10% of the studied oils then, the apparent polarity  $P$  of the oils increases in the order:

$$P_{\text{PLL}} < P_{\text{HDC}} < P_{\text{T22}} < P_{\text{T9}} < P_{\text{IPP}} = P_{\text{GTCC}} = P_{\text{PEH}} \ll P_{\text{DC}}$$

#### 4.2. Interfacial tension measurements

The polarity of oils has a direct influence on their interfacial tension with water: the higher the interfacial tension, the lower the oil polarity. The interfacial tension of the eight oils (PLL,

T22, T9, HDC, GTCC, IPP, PEH and DC) was measured and the results are presented in Table 2.

PLL showed the highest interfacial tension, whereas DC exhibited the lowest one. PLL can thus be considered as the less polar oil while DC would be the most polar oil of the whole studied oil series. It is important to note that for most oils, the interfacial tension varied with time. This variation was particularly significant for HDC and PEH for which, the difference in interfacial tension with time reached 7.7 and 8.8 mN/m, respectively. This parameter must be taken into account since it had a slight effect on the classification of oils based on their interfacial tension. Indeed, when the interfacial tension was measured immediately after contact between the two phases, it decreased in the order:  $\gamma_{\text{PLL}} > \gamma_{\text{T9}} > \gamma_{\text{T22}} > \gamma_{\text{HDC}} > \gamma_{\text{IPP}} > \gamma_{\text{PEH}} > \gamma_{\text{GTCC}} > \gamma_{\text{DC}}$ . However, after 10 h, the interfacial tension of the oil series varied in the order:  $\gamma_{\text{PLL}} > \gamma_{\text{T9}} > \gamma_{\text{T22}} > \gamma_{\text{HDC}} > \gamma_{\text{IPP}} > \gamma_{\text{GTCC}} > \gamma_{\text{PEH}} > \gamma_{\text{DC}}$ . Thus, for two of the studied oils (GTCC and PEH), the rank was inverted. This classification did not change after 20 h following the beginning of the experiments (Table 2).

#### 4.3. High-performance liquid chromatography

Reversed-phase HPLC is a unique tool to investigate the lipophilicity of xenobiotics and physico-chemical parameters such as the log  $P$  can be derived from retention data (Kaliszan et al., 2003). In such systems, the retention of a particular analyte depends on its penetration into the hydrocarbon layer and on its solubility in the mobile phase. According to Horvath's solvophobic theory, the surface tension is a key parameter of the mobile phase (Horvath et al., 1976). Using gradient elution, the polarity of the mobile phase is gradually changing from polar to non-polar. A linear gradient running from methanol to chloroform was used to ensure, as a primary objective, the elution of the eight oils within the gradient duration. These experimental conditions warrant a maximum analysis time of 30 min even for the less polar sample. As we already explained elsewhere (Gaudin et al., 2002), rapid linear gradients (i.e. 5% min<sup>-1</sup>) ensure a linear relationship between the retention time and the hydrocarbonaceous volume of a homologous series. To be accurate, the oils investigated in this study do not constitute a homologous series. However, it is thought that due to their structural similarity, the retention mechanism is similar for the eight oils and the same assumptions than in Gaudin et al. (2002) hold. Due to the linear shape of the gradient program, the retention time of a

Table 2  
Interfacial tension values measured for the 8 studied oils at 23 °C

Oil	$\gamma$ (mN/m) (at $t=0$ )	$\gamma$ (mN/m) (at $t=10$ h)	$\Delta\gamma_1$ (mN/m)	$\gamma$ (mN/m) (at $t=20$ h)	$\Delta\gamma_2$ (mN/m)
1-Decanol (DC)	8.5	8.3	0.2	8.3	0.2
Caprylic-capric triglyceride (GTCC)	25.4	23.2	2.2	21.8	3.5
Ethyl-2 hexyl pelargonate (PEH)	27.5	20.7	6.8	18.7	8.8
Isopropyl palmitate (IPP)	28.6	27.7	0.9	26.7	1.9
<i>n</i> -Hexadecane (HDC)	47.0	41.3	5.9	39.5	7.7
Naphtenic oil T22	47.3	43.4	4.0	42.0	5.3
Naphtenic oil T9	47.3	44.8	2.5	43.9	3.3
Liquid paraffin (PLL)	52.9	52.4	0.5	52.2	0.7

$\Delta\gamma_1$  is the difference between  $\gamma$  at  $t=0$  and  $\gamma$  at  $t=10$  h.  $\Delta\gamma_2$  is the difference between  $\gamma$  at  $t=0$  and  $\gamma$  at  $t=20$  h.

Table 3  
Retention times (Rt) for the eight studied oils

	1-Decanol (DC)	Ethyl-2 hexyl pelargonate (PEH)	Caprylic-capric triglyceride (GTCC)	Isopropyl palmitate (IPP)	<i>n</i> -Hexadecane (HDC)	T9	T22	Liquid paraffin (PLL)
Rt (major peak), min	3.2	5.9	6.7	7.1	10.2	11.2	11.4	12.7
Rt (minor peak), min						8.9	9.6	

particular oil is thus expected to be directly proportional to its polarity.

The retention times of the eight studied oils were determined by HPLC. The values are presented in Table 3 and illustrated in Fig. 2. The chromatograms for T9 and T22 showed two minor peaks in addition to their major peaks. The plots in Fig. 2 allowed classifying the oils, based on their retention time and thus on their partition between the C18 grafted stationary phase and the methanol:chloroform mobile phase. The longer the retention time, the lower the polarity of the oils. From the results in Fig. 2, it appears that the retention times (Rt) vary in the order:  $R_{tPLL} > R_{tT22} > R_{tT9} > R_{tHDC} > R_{tIPP} > R_{tGTCC} > R_{tPEH} > R_{tDC}$ .

## 5. Discussion

The polarity of the eight studied oils was evaluated using three different approaches, the dielectric constant requirement for their solubilization, the measurement of their interfacial tension with water (immediately and at equilibrium), and the determination of their retention time on an HPLC-C18 column. In Table 4, the classifications of the oils obtained by the three methods are compared.

Whereas, for five of the studied oils, PLL, IPP, GTCC, PEH, and DC, the ranks are identical whatever the method used, for HDC, T9 and T22, they may vary. Three points have been considered to explain these differences, such as the deviations from the mean weight percentage of dissolved oil in the solubilization experiments, the composition of the samples (deduced from the HPLC chromatograms) and the evolution of the surface tension with time.

Interestingly for HDC, T9 and T22, the mean weight percentages of solubilized oil varied from one experiment to another to a greater extent than for the other studied oils. The solubilization method thus showed that the behavior of these oils was less predictable than that of the others.

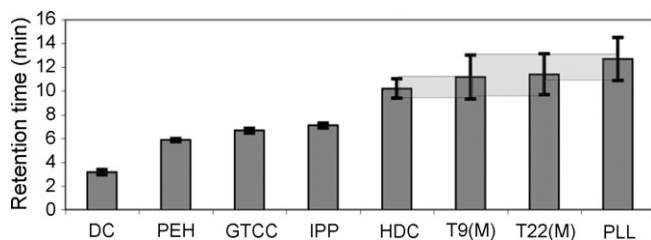


Fig. 2. Comparison of the retention times for the eight studied oils. For T9 and T22, only the major retention peaks are considered. The retention time overlapping zones are indicated.

A thorough analysis of the HPLC chromatograms provides information on the possible existence of structural analogs and impurities in the studied samples. As shown in Fig. 3 for PLL, the major peaks of the studied oils are often formed of several thin peaks more or less superimposed. These peaks most probably correspond to the elution of chemically related compounds present in the samples. PLL would thus be a mixture of closely related compounds and not a true chemical entity. This simultaneous elution has an impact on the value of the retention time measured at the distribution maximum.

In order to evaluate the influence of this distribution on the polarity value expressed as the retention time, the width at the base of the peaks (LB) was determined by taking into account all eluted components for each studied oil. For some of the studied oils an enlargement of the retention zone was observed. These data were added to Fig. 2. It is interesting to note that HDC, T22 and T9 are among the four oils that have the largest retention time overlapping zones. This might explain the discrepancies observed in the classification for these three oils (Table 4).

An extra feature of HPLC derives from its classical use by providing information on the possible presence of impurities as observed for T22 (Fig. 4) and T9. Thus, the chromatographic analysis of the oils allowed not only the evaluation of their polarity by the determination of their retention time but also provided information on their purity.

On this matter, interfacial tension measurements also provided useful additional information for the formulation of emulsions. The data in Table 2 show that for several of the studied oils, the interfacial tension varied with time. The significant decrease in  $\gamma$  (>3 mN/m) observed for HDC, T22, T9, GTCC

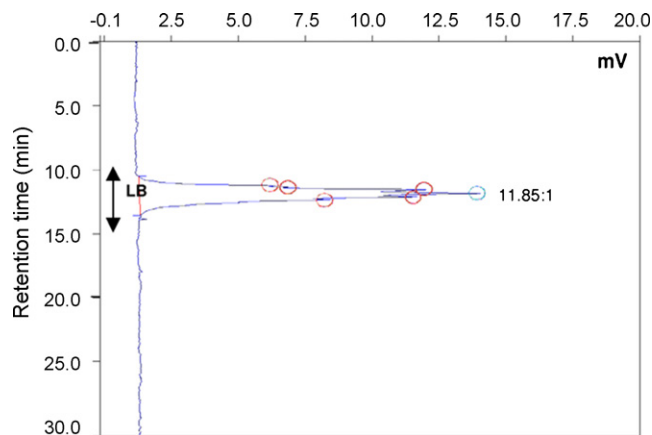


Fig. 3. PLL chromatogram showing major and minor peaks corresponding to the elution of chemically related compounds present in the oil sample. LB: width at the base of the peaks.

Table 4

Comparison of oil ranks in the three classifications of the studied oils (the less polar oil has the rank 1, the most polar one has the rank 8)

Rank	Oil rank from $\epsilon$ results	Oil rank from $\gamma$ results at equilibrium	Oil rank from RP-HPLC results
1	Liquid paraffin (PLL)	Liquid paraffin (PLL)	Liquid paraffin (PLL)
2	<i>n</i> -Hexadecane (HDC)	T9	T22
3	T22	T22	T9
4	T9	<i>n</i> -Hexadecane (HDC)	<i>n</i> -Hexadecane (HDC)
5	Isopropyl palmitate (IPP)	Isopropyl palmitate (IPP)	Isopropyl palmitate (IPP)
6	Caprylic-capric triglyceride (GTCC)	Caprylic-capric triglyceride (GTCC)	Caprylic-capric triglyceride (GTCC)
7	Ethyl-2 hexyl pelargonate (PEH)	Ethyl-2 hexyl pelargonate (PEH)	Ethyl-2 hexyl pelargonate (PEH)
8	1-Decanol (DC)	1-Decanol (DC)	1-Decanol (DC)

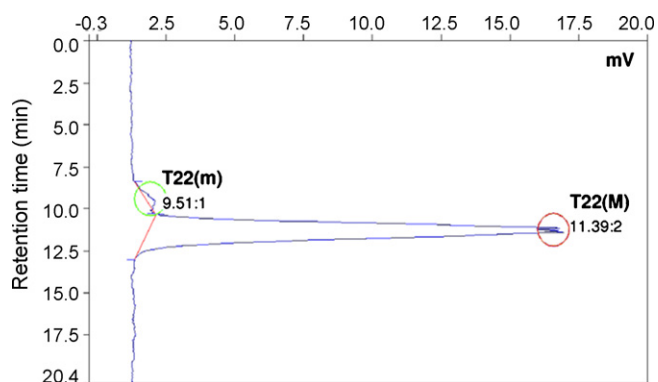
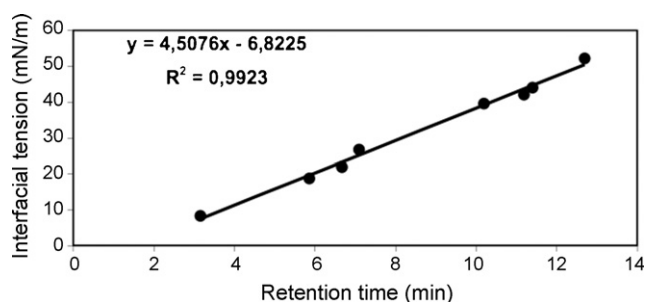


Fig. 4. Chromatogram of the T22 sample. T22M: major peak, T22m: minor peak.

and PEH could originate (a) from the presence of impurities (T22 and T9), (b) from the presence of chemical analogs (however, for PLL no significant change in the interfacial tension was observed), (c) from the slow solubilization of oil in water or water in oil, which would modify the polarity of both phases, and (d) from the interfacial rearrangement of oil molecules adsorbed at the interface. The latter could result from the complex chemical structure of some of the oils (GTCC, PEH).

The interfacial tension values at  $t = 20$  h were compared to the retention times obtained from the chromatograms. Interestingly, the comparison of the interfacial tension with the retention times proved to be linear (Fig. 5).

Using these two techniques, it was thus possible to determine the polarity of oils, and moreover, to get additional information on the oil composition and purity, and on the interfacial behavior of oils with time. The latter information is interesting for emulsion formulation because oil and surfactant may interact at the

Fig. 5.  $\gamma$ -Rt relationships for the eight studied oils.

interface and this interaction in turn might affect the stability with time of the emulsions formed (Cournarie et al., 2004).

## 6. Conclusion

Compared to the solubilization method, HPLC and interfacial tension measurements appeared more reliable for the determination of oil polarity. They are less fastidious and provide thorough information on the system. The chromatographic analysis is faster than the other methods, does not require large oil samples and show the presence of impurities and related compounds. However, it is only a comparative method and requires calibration. Compared to the former, the interfacial tension measurement is a quantitative method that gives a direct evaluation of oil polarity, and information on the interfacial behavior of oil with time. The coupling of the two methods provides useful information on the oils and allows predicting their behavior in the formation and stability of simple and multiple emulsions.

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