

## IGC studies of binary cationic surfactant mixtures

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### Abstract

Inverse gas chromatography (IGC) has been used to measure the interaction parameter between two twin-tailed cationic surfactants. Dido-decyltrimethylammonium (DDAB) and dioctadecyltrimethylammonium (DODAB) bromides and their mixtures were used as stationary phases. IGC and DSC techniques have been used for the determination of the temperature zone of working. The activity coefficients at infinite dilution (on a mole fraction basis) were calculated for eleven probe solutes on each pure surfactant column. Values of interaction parameter between surfactants obtained at four weight fractions of the mixtures and at five temperatures are positive and suggested that the interactions is more unfavourable with the increment of DODAB concentration in the mixture. The results are interpreted on the basis of partial miscibility between DDAB and DODAB.

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### 1. Introduction

The homologous double-chained liposome-forming cationic lipids dioctadecyltrimethylammonium bromide (DODAB) and didodecyltrimethylammonium bromide (DDAB) have been some of the most investigated cationic lipids [1–5] but there is scarce literature on the phase behaviour of mixtures of these surfactants. Lipid mixtures in solution can be used for monitoring their structure and phase behaviour suitable for specific applications in science and technology. Such applications may require well-controlled properties [6].

The difference in chain length of these lipids ( $C_{18}$  and  $C_{12}$ ) yields interesting characteristics to the behaviour of solutions of their mixtures which merits investigation on the interactions along the mixtures composition variation.

The formation of surfactant molecules aggregates such as spherical, rod-like or globular micelles, vesicles/liposomes, mesophases, etc., depend on the molecular characteristics of surfactants. The size of aggregates, architecture and confor-

mation of the chains depend on the Gibbs free energy of the system. The total energy results from the two main factors, the repulsive energy between polar heads and the attractive energy from the packing of hydrocarbon chains (hydrocarbon/water repulsion and van der Waals interaction between chains). These factors are not only applicable for pure surfactants but for mixtures, too.

For bicationic surfactant mixtures such as DDAB and DODAB, the polar head is the same and a non-synergic behaviour is expected. However, there are in literature several examples of steric hindrances in the hydrocarbon core that cause non-ideal behavior [7,8], even in mixtures of homologous surfactants [9].

Inverse gas chromatography (IGC) has been used in the characterisation of physicochemical properties of a number of liquid and solid materials [10–16]. This dynamic methodology has shown that measurements made under strictly controlled experimental condition would give thermodynamic information [17].

The term inverse means that the substance under study is placed as the stationary phase in a chromatographic column and the retention of a series of probe solutes is measured. The physicochemical parameters calculated from the retention data

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describe the molecular interactions between the studied material and the solutes. An advantage of this method is that it can be directly applicable for mixtures. Thus the polymer–polymer interaction parameter  $\chi_{23}$  for miscible polymer mixtures was determined [18,19], although these values were different for each probe solute sample employed.

It was demonstrated that the dependence of  $\chi_{23}$  on the solvent nature obtained by IGC basically is owed to the additive approximation of Flory–Huggins theory. Moreover, under certain conditions  $\chi_{23}$  values could be obtained independently of the solute samples [20,21]. This method has been also applied to mixtures of polymers with compounds of small non volatile molecules, such as plasticisers and liquid crystals [22,23]. IGC has been employed for the characterisation of the thermodynamic behaviour of liquid crystals [24] through the activity coefficients, enthalpies and entropies involved in the dissolution process. Price and Shillcock [25] reported a study of the behaviour of siloxane-cyanobiphenyls with low molar mass. They also determined activity coefficients and interaction parameters of these liquid crystals [26].

DDAB is a pure double-tailed cationic surfactant that forms two lamellar phases with water that coexist at room temperature [27,28]. DODAB is also a twin-tailed cationic surfactant. The phase diagram of DODAB–water system at room temperature shows crystals of composition DODAB·2H<sub>2</sub>O and isotropic solution [29].

In a previous study [30,31] we determined solubility parameters and HLB values of cationic surfactants.

This paper is an attempt at characterising DODAB and DDAB mixtures from a physicochemical point of view, through the interactions between the double hydrocarbon tails of both cationic surfactants obtained by IGC from retention data of the pure components and their mixtures. These studies permit determination of the interaction parameter of such surfactant mixtures.

## 2. Experimental

### 2.1. Materials

Didodecyldimethylammonium bromide (DDAB) and dioctadecyldimethylammonium bromide (DODAB) (Sigma, analytical grade) were used as received. All probe solvents (Merck) were 99% or better.

### 2.2. Differential scanning calorimetry

DSC was performed on a Perkin Elmer DSC 6 calorimeter, between 20 and 250 °C, with a scanning rate of 10 °C min<sup>-1</sup> and using samples of 5–10 mg for pure surfactants and 10–15 mg for materials collected over chromatography support. The instrument was calibrated with indium.

### 2.3. Inverse gas chromatography

Pure DDAB and DODAB and their mixtures were used as stationary phase and deposited on Chromosorb W, NAW, 60/80,

Table 1

Sorption heat (kJ mol<sup>-1</sup>) and standard deviation of different probe solutes in DDAB and DODAB

	DDAB	DODAB
<i>n</i> -Hexane	28.7 ± 0.3	30.7 ± 0.3
<i>n</i> -Heptane	33.4 ± 0.4	34.8 ± 0.4
<i>n</i> -Octane	38.6 ± 0.2	39.3 ± 0.3
Benzene	33.5 ± 0.2	33.7 ± 0.4
Toluene	37.5 ± 0.4	37.6 ± 0.2
Cyclohexane	29.8 ± 0.4	31.1 ± 0.2
Methylcyclohexane	33.6 ± 0.2	33.6 ± 0.2
Dichloromethane	33.2 ± 0.3	32.3 ± 0.3
Trichloromethane	43.8 ± 0.4	43.4 ± 0.2
Carbon tetrachloride	35.5 ± 0.2	34.3 ± 0.2
Ethyl acetate	33.3 ± 0.3	32.6 ± 0.1

which was employed as solid support. The column filler was prepared using methanol as solvent in a rotary evaporator under a flow of dry nitrogen and was kept in a dry atmosphere before filling the columns (inoxidable steel pipes). The column was loaded and conditioned for 1 h at 90 °C under a flow of carrier gas. The amount of stationary phase on the support was determined by calcinations on about one g of material. The data employed in the specific retention volume computation were obtained by using a column 100 cm long, 1/4 inch external diameter, and the packing characteristics are included in supplementary material (Table 1).

The retention time measurement for each solute was performed with a Hewlett Packard, HP 6890 series, GC System, equipped with a flame ionization detector (FID). Column temperature was measured in a range between 363.15 and 403.15 K with an Iron-Constantan thermocouple placed in the direct environment of the column. The temperature stability during experiments was of ±0.2 K. The employed solutes were *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, methylcyclohexane, benzene, toluene, ethyl acetate, dichloromethane, trichloromethane and carbon tetrachloride.

Nitrogen was used as carrier gas. Flow rates were measured at the beginning of each experiment with an air-jacketed soap film flowmeter placed at the outlet of the detector. Inlet pressures were measured with a micrometry syringe (through the injector septum) which was connected to an open branch mercury manometer. To ensure that the results were independent of sample size and flow rate and those measurements were being made at infinite dilution the usual checks were made [32].

Solutes were injected with 10 µl Hamilton syringes, as steam in equilibrium with pure liquid. For all the solutes and for all the range of stationary phase concentrations the peaks were symmetric. The injector was kept at 150 °C and the detector at 180 °C.

Retention times ( $t_R$ ) were measured with a Chem Station system and the retention specific volumes ( $V_g^0$ ) were calculated with the following relationship [32]:

$$V_g^0 = j(F_f/w)(273.15/T_f)(t_R - t_0)(p_0 - p_w)/p_0, \quad (1)$$

where  $j$  is the James–Martin compressibility correction factor,  $p_0$  represents the outlet column pressure,  $F_f$  is the flow rate measured at pressure  $p_0$  and temperature  $T_f$ ,  $w$  is the mass of

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