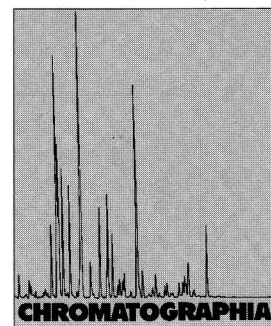


# Solubility Parameter Determination of Cationic Surfactants by Inverse GC



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## Key Words

Gas chromatography  
Inverse gas chromatography  
Cationic surfactants  
Solubility parameter

## Summary

The solubility parameters of cationic surfactants were obtained using the inverse gas chromatographic technique. The surfactants didodecyl dimethyl ammonium bromide, dioctadecyl dimethyl ammonium bromide and dodecyl pyridinium chloride were used as stationary phase and retention data of different probe solutes were measured at different temperatures. The results were analysed by the combination of Flory-Huggins and Hildebrand theories, and the solubility parameters of the surfactants were obtained in a range of temperatures between 80–120 °C.

## Introduction

Solubility parameters have not been exhaustively used in the characterisation of surface active agents in spite of the fact that the theory discusses the behaviour of emulsifiers in water/oil (W/O) systems in terms of the density of cohesive energy of the system components [1, 2].

Inverse gas chromatography has been used in the characterisation of physicochemical properties of a number of liquid and solid materials [3–8]. The term inverse gas chromatography means that the substance under study is placed in a chromatographic column as the stationary phase and the retentions of a series of test solutes are measured. The physicochem-

ical parameters calculated from the retention data describe the molecular interactions between the studied material and the solutes.

In this paper, inverse gas chromatography was used to determine solubility parameters of cationic surfactants of didodecyl dimethyl ammonium bromide (DDDAB), dioctadecyl dimethyl ammonium bromide (DODDAB) and dodecyl pyridinium chloride (DPC). Our purpose was to obtain the Hydrophilic-Lipophilic Balance (HLB) values with the solubility parameters for these cationic surfactants and to examine the possibility that they show a behaviour similar to a non-ionic and anionic surfactants.

## Theoretical Relationships

Solubility parameters of a volatile compound can be calculated by the basic equation:

$$\delta = \left( \frac{\Delta H_v - RT}{v_1^0} \right)^{1/2} \quad (1)$$

where  $\Delta H_v$  is the enthalpy of vaporization,  $R$  is the gas constant,  $T$  is the absolute temperature and  $v_1^0$  is the molar volume.

For low volatility or non-volatile species, the use of this equation is not possible and alternative methods must be used.

DiPaola-Baranyi [9, 10] presented a procedure for the evaluation of the solubility parameter of polymeric substances that uses the solute-solvent interaction parameter  $\chi_{1,2}^\infty$  obtained from the Scatchard Hildebrand theory [1]. They used the following expression:

$$\chi_{1,2}^\infty = \frac{v_1^0(\delta_1 - \delta_2)^2}{RT} + \chi_s^\infty \quad (2)$$

where  $\delta_1$  and  $\delta_2$  are the solubility parameters of the solute and the solvent and  $\chi_s^\infty$  is the entropic factor of the interaction parameter.

Dividing this expression into  $v_1^0$  it is possible to obtain the following expression:

$$\frac{\delta_1^2}{RT} - \frac{\chi_{1,2}^\infty}{v_1^0} = \left( \frac{2\delta_2}{RT} \right) \delta_1 - \left( \frac{\delta_2^2}{RT} + \frac{\chi_s^\infty}{v_1^0} \right) \quad (3)$$

Plotting the left hand side of equation (3) against  $\delta_1$  it is possible to obtain  $\delta_2$  for the

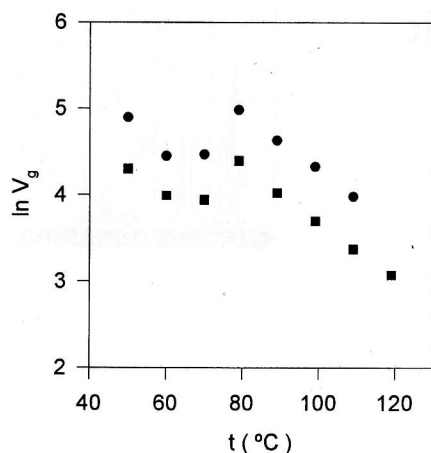


Figure 1. Retention vs. temperature. Toluene (●); n-Octane (■).

non-volatile material from the slope of the resulting straight line.

The specific retention volume  $V_g$  is characteristic of a particular solute, stationary phase, and a carrier gas. It is the net retention volume at 0 °C for unit weight of stationary phase and is given by:

$$V_g = \frac{273.15 V_N}{wT} \quad (4)$$

where  $w$  is the mass of stationary phase in grams present in the column,  $V_N$  is the net retention volume and  $T$  is the column temperature.

The solute solvent interaction parameter,  $\chi_{1,2}^\infty$ , from Scatchard Hildebrand theory and the specific retention volume from chromatography are related by:

$$\chi_{1,2}^\infty = \ln \left[ \frac{273.15R}{p_1^0 V_g^0 M_1} \right] - \frac{p_1^0 (B_{11} - v_1^0)}{RT} \quad (5)$$

where  $p_1^0$ ,  $M_1$  and  $v_1^0$  stand for vapour pressure, molar mass and molar volume of the solute, respectively.  $B_{11}$  is the second virial coefficient for solute-solute interactions in the vapour phase.

## Experimental

DDDAB, DODDAB and DPC were used as stationary liquids and Chromosorb, W, NAW, 60/80, was used as solid support in all cases. The surfactant was dissolved in methanol for preparing the stationary phases. The columns prepared with DDDAB (melting zone about 75 °C) as stationary phase were 180 cm in length and 3.2 mm in external diameter with

Table I. Specific retention volume at 100 °C, solution enthalpy, activity coefficient and interaction parameters values of different solutes in DDDAB.

Solute	$V_g^0$ ( $\text{cm}^3 \text{g}^{-1}$ )	$\Delta H_k \pm \sigma$ ( $\text{kJ mol}^{-1}$ )	$\Omega_1^\infty$	$\chi_{1,2}^\infty$
n-Hexane	9.855	$29.4 \pm 0.2$	11.97	2.48
n-Heptane	19.59	$35.1 \pm 1.1$	11.55	2.45
n-Octane	38.82	$37.8 \pm 0.2$	11.32	2.43
Cyclohexane	20.28	$31.2 \pm 0.4$	8.11	2.09
Methylcyclohexane	29.66	$34.1 \pm 0.7$	8.28	2.11
Benzene	36.96	$33.4 \pm 0.3$	4.55	1.51
Toluene	69.43	$39.1 \pm 0.9$	4.95	1.60
Dichloromethane	22.94	$32.2 \pm 0.8$	2.22	0.80
Trichloromethane	88.27	$45.6 \pm 0.2$	0.75	-0.28
Carbon tetrachloride	35.62	$35.5 \pm 0.3$	2.24	0.81
Ethyl acetate	14.62	$32.1 \pm 0.6$	9.72	2.27

1.6739 g packing with 9.90% "liquid" phase (Column A1). Column (B1) also with DDDAB was 100 cm in length and 6.3 mm in external diameter with 7.9285 g packing with 9.04% "liquid". Column B2 packed with DODDAB (melting zone about 84 °C) as stationary phase was 100 cm in length with 7.3291 g packing with 9.00% "liquid" and the column packed with DPC (melting zone about 64 °C), also of 100 cm in length (B3) contained 7.6780 g of packing with 9.89% "liquid". The packings were kept in a dry atmosphere before filling the columns.

The chromatographic measurements were performed in a Perkin-Elmer, Sigma 300, gas chromatograph with a thermal conductivity detector using hydrogen as carrier gas. The solutes were injected with a 50  $\mu\text{L}$  Hamilton syringe as vapour in equilibrium with pure liquid.

The retention times ( $t_R$ ) were measured with an electronic integrator Perkin-Elmer, LCI100, and the specific retention volumes were calculated with the expression:

$$V_g^0 = j(F_0/w)(273.15/Tf)(t_R - t_M) \quad (6)$$

$$(p_0 - p_w)/p_0$$

where  $j$  is the James-Martin compressibility correction factor,  $p_0$  represents the outlet column pressure,  $F_0$  is the flow rate measured at pressure  $p_0$  and at temperature  $T_f$ ,  $p_w$  is the water vapour pressure at  $T_f$ , and  $t_M$  is the dead time of the column which was measured using the air peak obtained from the thermal conductivity detector.

## Results and Discussion

The retention of some test solutes using column A<sub>1</sub> was performed. DDDAB has a melting zone between 70–80 °C. Below this temperature the solute is not expected to penetrate the surfactants and the only retention mechanism involved would be the absorption at the gas-solid interface.

From 50 °C, the values of  $\ln V_g^0$  decrease linearly with the temperature until 70 °C. At this temperature a change in the retention is produced. Melting point determination could be performed studying the retention of a solute against the temperature in 70–80 °C zone. Above 80 °C the behaviour is characteristic of a process where the predominant retention mechanism is the partition of the solute in the stationary phase as can be seen in Figure 1.

A study of the effect of the gas flow rate on the retention at 80 °C with column A<sub>1</sub> was made. There was no appreciable effect on the specific retention volume of a test solute when carrier gas flow varied between 20 and 80  $\text{mL} \cdot \text{min}^{-1}$ .

The retention data used to calculate the solubility parameter of surfactants were determined for the solutes in Table I using column B1. Table II gives the parameter calculated using retention data obtained from column B2 and in Table III from column B3. All the retention measurements were made between 80 and 120 °C and with a flow approximately equal to 40  $\text{mL} \cdot \text{min}^{-1}$ .

The heats of solution ( $\Delta H_k^0$ ) were calculated using the following expression:

$$\ln V_g^0 = \frac{\Delta H_k^0}{RT} + cte \quad (7)$$

The heats of solution correspond to a process of transfer of one mole of solute from an ideal gaseous phase at a pressure of 1 atmosphere to a hypothetical solution of unit molar fraction with the interactions of an infinitely diluted solution [11].

The  $(\Delta H_k^0)$  values obtained, as well as their respective standard deviations, were calculated using the Marquardt-Levenberg algorithm [12] and they are included in the respective tables for each surfactant studied.

Instead of  $\gamma^\infty$ , the infinite dilution molar fraction activity coefficient,  $\Omega^\infty$ , expressed as fraction weight is used throughout this work because the surfactant molecular weights ( $M_S$ ) are unknown. Where  $M_S$  is available the two activity coefficients are related by:

$$\frac{\Omega^\infty}{\gamma^\infty} = \frac{M_S}{M_1} \quad (8)$$

The activity coefficients at infinite dilution were estimated according to Patterson et al. [13] by:

$$\ln \Omega^\infty = \ln \left( \frac{273.15R}{p_1^0 v_g^0 M_1} \right) - \frac{p_1^0 (B_{11} - v_1^0)}{RT} \quad (9)$$

where  $p_1^0$ ,  $M_1$  and  $v_1^0$  stand for vapour pressure, molar mass and molar volume respectively.  $B_{11}$  is the second virial coefficient for solute-solute interactions in the vapour phase. The vapour pressures were calculated using Antoine equations and the coefficients were taken from Riddick, Bunger and Sakano [14]. The solute densities at different temperatures were estimated from Dreisbach's compilation [15]. The second virial coefficient of the solutes were calculated by Tsonopoulos's correlation using critical constants tabulated in Reid et al. [16].

The  $\chi_{1,2}^\infty$  values obtained from the chromatographic data at 100 °C have been included in Tables I, II, and III. These values allowed an estimation of the solubility parameter  $\delta_2$  of the DDDAB, DODDAB and DPC cationic surfactants using Eq. (3). Plotting the left hand term of this expression against the solubility parameter of solvents ( $\delta_1$ ), gave the slope to calculate the  $\delta_2$  parameter of the surfactant. The  $\delta_1$  values were calculated at different temperatures using the derivative expression of Haggmacher [17]. The critical constants of Antoine's equation were obtained from references (14) and (16).

Tables I, II and III show that the heats of solution for all the solutes have devia-

**Table II.** Specific retention volume at 100 °C, solution enthalpy, activity coefficient and interaction parameters values of different solutes in DODDAB.

Solute	$V_g^0$ (cm <sup>3</sup> g <sup>-1</sup> )	$\Delta H_k \pm \sigma$ (kJ mol <sup>-1</sup> )	$\Omega_1^\infty$	$\chi_{1,2}^\infty$
n-Hexane	13.15	30.3 ± 0.3	8.97	2.19
n-Heptane	26.54	37.9 ± 2.1	8.52	2.14
n-Octane	53.36	38.1 ± 0.2	8.23	2.11
Cyclohexane	25.54	30.5 ± 0.1	6.39	1.85
Methylcyclohexane	39.24	33.1 ± 0.5	6.26	1.83
Benzene	39.07	32.6 ± 0.2	4.30	1.46
Toluene	77.28	36.7 ± 0.2	4.45	1.49
Dichloromethane	25.20	31.6 ± 0.6	2.02	0.70
Trichloromethane	81.29	45.3 ± 1.1	0.81	-0.21
Carbon tetrachloride	38.02	33.5 ± 0.2	2.11	0.74
Ethyl acetate	14.25	31.4 ± 0.2	9.53	2.25

**Table III.** Specific retention volume at 100 °C, solution enthalpy, activity coefficient and interaction parameters values of different solutes in DPC.

Solute	$V_g^0$ (cm <sup>3</sup> g <sup>-1</sup> )	$\Delta H_k \pm \sigma$ (kJ mol <sup>-1</sup> )	$\Omega_1^\infty$	$\chi_{1,2}^\infty$
n-hexane	9.46	27.2 ± 0.1	14.32	2.66
n-heptane	18.66	32.2 ± 0.1	13.99	2.64
n-octane	36.03	36.4 ± 0.1	14.00	2.64
Cyclohexane	18.79	28.6 ± 0.1	10.03	2.31
Methylcyclohexane	28.44	30.9 ± 0.1	9.91	2.29
Benzene	39.51	31.9 ± 0.1	4.88	1.59
Toluene	74.90	36.8 ± 0.1	5.37	1.68
Dichloromethane	25.93	30.6 ± 0.1	1.57	0.45
Trichloromethane	153.6	39.3 ± 0.1	0.36	-1.02
Carbon tetrachloride	40.35	30.8 ± 0.1	2.20	0.79
Ethyl acetate	17.95	30.4 ± 0.1	9.01	2.20

tions of less than 2%, with values below 1% in most cases. The heat of solution of the different solutes in DODDAB are higher than those in DDDAB which in turn are higher than those in DPC.

The highest deviations from ideality correspond to solutes in DPC. The intermediate deviations correspond to solutes in DDDAB and the lowest to solutes in DODDAB. In all cases the chloromethanes give low values of  $\Omega^\infty$  which is less than unity for trichloromethane in all the surfactants. This corresponds to the negative values of the interaction parameter for these solutes in the three stationary phases.

Using the left hand term of Eq. (3) and the solubility parameter of the solvents ( $\delta_1$ ), we obtain the solubility parameter of the surfactant  $\delta_2$ . If we use all the solutes in Table I in the regression, we obtain a correlation coefficient of 0.88 with the chloromethanes aligned between them. If the chloromethanes (trichloromethane, dichloromethane and carbon tetrachloride) are discounted in the regression, we obtain a correlation coefficient higher than 0.96 for all the temperatures. The same characteristic is observed if we use the values in Table II for DODDAB and in Table III for DPC. In these cases,

the correlation coefficient of 0.91 with all the solutes included is poorer than 0.97 if the chloromethanes are excluded.

In Figure 2 the left hand term of Eq. (3) is plotted against the solubility parameter of the solutes used, except for the chloromethanes with DODDAB as the stationary phase.

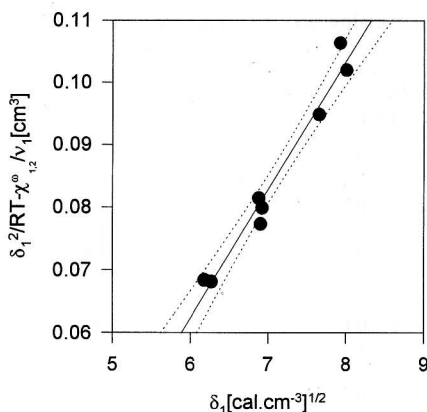
The solubility parameter of the surfactant  $\delta_2 = 6,8 \pm 0,5$  (cal mol<sup>-1</sup>)<sup>1/2</sup> has been calculated from the values of the slope obtained for the different solutes for DODDAB at 100 °C.

From the values at all the other temperatures it is possible to express the dependency of  $\delta_2$  with the temperature in °C by the equation:  $\delta_2 = 8.2563 - 0.0143 \cdot t$ . From the extrapolation at 25 °C the value of  $\delta_2$  is 7.90 (cal mol<sup>-1</sup>)<sup>1/2</sup>.

For DODDAB, using the values in Figure 2, the solubility parameter,  $\delta_2$ , at 100 °C is  $7,1 \pm 0,6$  (cal mol<sup>-1</sup>)<sup>1/2</sup>.  $\delta_2$  at 25 °C is 11,58 (cal mol<sup>-1</sup>)<sup>1/2</sup> from the equation  $\delta_2 = 12.8515 - 0.0510 \cdot t$ .

For DPC the solubility parameter,  $\delta_2$ , of the surfactant at 100 °C is  $7.06 \pm 0.5$  (cal mol<sup>-1</sup>)<sup>1/2</sup>. The equation  $\delta_2 = 8.3540 - 0.0129 \cdot t$  gives a value of 8.03 (cal mol<sup>-1</sup>)<sup>1/2</sup> at 25 °C.

Little [18], presented a correlation between the solubility parameter of surfac-



**Figure 2.** Solubility parameter of DODDAB obtained from  $\chi_{1,2}^{\infty}$  parameter calculated from chromatographic data at 100 °C.

tants and the Hydrophile-Lypophile Balance (HLB). He obtained solubility parameters calculated for non-ionic surfactants using the Hildebrand's rule and the respective values of HLB taken from the bibliography. The method of Little [18] was proved applicable for non-ionic and anionic surfactants. For all the cationic systems studied in this paper, we obtained different values from those calculated in the bibliography and even a negative value in one case.

## Conclusions

The solubility parameters of cationic surfactants were obtained using inverse gas

chromatography. There appear to be no data available in the literature to compare with our results. For all the cationic systems studied, the method of Little [18] was proved to be not applicable for these surfactants.

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## References

- [1] Hildebrand, J.H.; Scott, R.L. "The solubility of nonelectrolytes", 3<sup>rd</sup> edn., Reinhold, New York, 1950.
- [2] Little, R.C. *J. Colloid Interface Sci.* **1966**, *21*, 266–272.
- [3] Fernández Sánchez, E.; Fernández Torres, A.; García Domínguez, J.A.; López de Blas, E. *J. Chromatogr. A* **1993**, *655*, 11–19.
- [4] Danner, R.P.; Tihminlioglu, F.; Surana, R.K.; Duda, J.L. *Fluid Phase Equilib.* **1998**, *148*, 171–188.
- [5] Jagiello, J.; Papirer, E. *J. Colloid Interface Sci* **1991**, *142*, 232–235.
- [6] Tian, M.; Munk, P. *J. Chem. Eng. Data* **1994**, *39*, 742–755.
- [7] Kamdem, D.P.; Riedl, B. *J. Colloid Interface Sci.* **1992**, *150*, 507–516.
- [8] Voelkel, A.; Janas, J.; García Domínguez, J.A. *J. Chromatogr. A* **1993**, *654*, 135–141.
- [9] Di Paola-Baranyi, G.; Braun, J.M.; Guillet, J.E. *Macromolecules* **1978**, *11*, 224–229.
- [10] Di Paola-Baranyi, G.; Guillet, J.E. *Macromolecules* **1978**, *11*, 228–232.
- [11] Meyer, E.F. *J. Chem. Educ.* **1973**, *50*, 191–194.
- [12] Marquardt, D.W. *J. Soc. Appl. Mat.* **1963**, *2*, 431–435.
- [13] Patterson, D.; Tewari, Y.B.; Schreiber, H.P.; Guillet, J.E. *Macromolecules* **1971**, *4*, 356–359.
- [14] Riddick, A.R.; Bunger, W.B.; Sakano, T.K. "Organic Solvents. Techniques of Chemistry", 4<sup>th</sup> Ed., Wiley-Interscience, New York, 1986.
- [15] Dreisbach, R.R. *Advances Chemistry Series*, publishing by A.C.S., 1955.
- [16] Reid, R.C.; Prausnitz, J.M.; Sherwood, T.K. "The properties of Gases and Liquids", 3<sup>th</sup> Ed. McGraw-Hill, New York, 1977.
- [17] Hoy, K.L. "The Hoy, Tables of Solubility Parameters, Solvents & Coatings Materials", S. Charleston, W. Virginia 25303, 1985.
- [18] Little, R.C. *J. Colloids Interface Sci.* **1978**, *65*, 587–588.

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