CONCURRENT SOLUTION AND ADSORPTION OF HYDROCARBONS IN GAS CHROMATOGRAPHIC COLUMNS PACKED WITH DIFFERENT LOADINGS OF 3-METHYLSYDNONE ON CHROMOSORB P

ADSORCION Y DISOLUCION SIMULTANEA DE HIDROCARBUROS EN COLUMNAS DE CROMATOGRAFIA GASEOSA RELLENAS CON DIFERENTES CARGAS DE 3-METILSYDNONA SOBRE CHROMOSORB P

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SUMMARY

Thermodynamic properties of solution in 3-methylsydnone (3MS) and of adsorption at the nitrogen/3MS interface were gas chromatographically measured for a group of fifteen hydrocarbons at infinite dilution conditions. Retention volumes were measured at five temperatures within the range 37-52°C in six columns containing different loadings of 3MS on Chromosorb P AW. Partition and adsorption coefficients were calculated and from their temperature dependence the corresponding enthalpies were obtained, although with considerable error; infinite dilution activity coefficients of the hydrocarbons in the bulk and in the surface phases demonstrated an strong correlation. Bulk activity coefficients in 3MS were very much smaller than those previously measured for the same solutes in formamide (FA) and in ethyleneglycol (EG), and were also smaller than what could be predicted on account of 3MS cohesive energy density as estimated from the quotient $\sigma/v^{1/3}$ *(*σ*: surface tension; v: molar volume). There was not such a large difference between the surface activity coefficients in the three solvents; furthermore, the quotients (surface activity coefficient/bulk activity coefficient) for a given solute in 3MS were twice as large as in FA and about three times larger than in EG. These results make evident the difficulties inherent in the prediction of surface phase properties from those in the bulk, and cast doubts on the pertinency of employing the surface tension to compare cohesive energy densities of polar solvents with important chemical differences.*

Keywords: *3-methylsydnone; adsorption; solution activity coefficients; surface activity coefficients; gas chromatography; chromatography thermodynamics* .

INTRODUCTION

3-Methylsydnone (3MS) is a polar solvent with some interesting properties; conspicuous among these are the large values of its dielectric constant and of its dipole

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moment. Some of its physical properties are given in Table 1 together with the corresponding values for formamide (FA) and ethyleneglycol (EG), two solvents that shall be compared with 3MS in the present paper. While FA and EG are highly associated liquids, 3MS is aprotic and the value of its Kirkwood *g* factor is 1.1 [1], indicating a random distribution of the molecular dipoles. However the cohesive energy density (c.e.d) of 3MS measured by the quotient $\sigma/v^{1/3}$, as proposed by Gordon [2], is apparently very high and intermediate between those of FA and EG.

Table 1

Physical Properties of Solvents

	EG, 25°C	FA, 25°C	3MS, 40°C
Dielectric Constant, ε	37.7^{a}	$105.^{a}$	144^{c}
Dipole Moment, μ (D)	2.28^{a}	3.73^{a}	7.3^{d}
Surface Tension, σ (dyn/cm)	$46.^{b}$	57.9^{b}	$57.^{e}$
Refractive Index, n^D	1.4306^{b}	1.4468^{b}	1.5150^{c}
Viscosity, η (cp)	16.2^{a}	3.30^{a}	5.50^{c}
Molar Volume, v (cm^3/mol)	55.92^{b}	39.89^{b}	76.49^{c}
$\sigma/v^{1/3}$ (dyn/cm^2)	12.0	16.9	13.4

[a] "Handbook of Chemistry and Physics", 68th. ed. The Chemical Rubber Co., Cleveland, OH, 1988.
[b] Riddick, J. A., and Bunger, W. B.."Organic Solvents". Wiley-Interscience, New York, 1970.
[c] Reference (1)
[d] Schmid. G. H., *J. Mol. Struct.* 5, 236 (1970).
[e] Reference (3).

On account of its high dielectric constant and c.e.d., 3MS was a good candidate to promote amphiphilic aggregation. But Evans and collaborators [3] were unable to detect formation of micelles in this solvent, a fact that these authors associated with the absence of hydrogen bonding in 3MS. This made the measurement of free energies of solution of hydrocarbons in 3MS interesting since, as Evans pointed out, they are intimately related to the driving force for surfactants aggregation. This interest was reinforced by the lack of information about the solvent properties of 3MS.

Gas chromatography, using 3MS as the stationary phase, offers a series of advantages for these measurements. In the first place because chromatographic measurements can be effectively done at infinite dilution of the solute in the stationary phase. In the second place because a considerable gas-liquid interface is generated when the stationary phase is coated on a porous solid; for a polar liquid like 3MS, in which the hydrocarbons shall display important positive deviations from the ideal solution behavior, a mixed retention mechanism can be predicted: partition in the bulk liquid and adsorption on the gas-liquid interface [4-6]. Using adequate conditions the thermodynamic parameters characteristic of both processes can be simultaneously determined. Finally the measurements can be performed over a range of temperatures, and partition and adsorption enthalpies may be evaluated [7], although with considerable uncertainties because of the indirect nature of the calculation

The retention behavior of fifteen hydrocarbons representative of different families was measured in the present work at five temperatures equally spaced within the range 37-52°C, in six columns containing different concentrations of 3MS in their packings. Experimental results are treated according with well established theoretical chromatographic principles.

MATERIALS AND METHODS

3MS was synthesized from N-methylglycine by the method of Vasil'eva and Yashunskii [8]. N-nitroso-N-methylglycine was extracted with ether, during 36 h, in a liquid-liquid extraction apparatus; the extract was dried with magnesium sulfate and the ether was vacuum distilled. The intermediate was then reacted with acetic anhydride (5.5 moles per mole of N-methylglycine) for ten days in the dark at room temperature. Excess acetic anhydride was removed under vacuum using toluene to remove the last traces, and 3MS was distilled twice under vacuum (145°C / 0.25 Torr), a 20 cm Vigreaux column being intercalated in the second opportunity. The product thus obtained was lightly yellow, melted at about 36°C and its IR spectrum was coincident with that appearing in ref. 3. Hydrocarbon solutes of different origins, all of them more than 99% pure, were used as received; their names can be read in Table 2.

Table 2

Thermodynamic functions of partition and adsorption of hydrocarbons at infinite dilution in 3-Methylsydnone at 40°C

SOLUTE	$K_L \pm \sigma(K_L)$	$-\Delta H_L^\circ$ (KJ/mol)	$K_A \pm \sigma(K_A)$ ($\times 10^4$ cm)	$-\Delta H_A^\circ$ (KJ/mol)
n-Heptane	9.98 ± 0.22	25.7 ± 2.6	3.46 ± 0.01	33.9 ± 1.3
n-Octane	19.8 ± 0.47	30.4 ± 3.5	9.11 ± 0.02	38.8 ± 1.7
n-Nonane	41.3 ± 2.02	37.8 ± 7.6	24.0 ± 0.11	42.8 ± 2.3
n-Decane	108. ± 12.0	44.9 ±18.5	61.0 ± 0.63	46.8 ± 3.0
2,2,4-Trimethylpentane	9.75 ± 0.39	29.4 ± 4.4	4.43 ± 0.02	33.5 ± 1.3
Methylcyclohexane	21.5 ± 0.20	21.9 ± 1.3	2.58 ± 0.01	31.6 ± 1.1
Ethylcyclohexane	46.0 ± 0.96	27.0 ± 2.7	6.66 ± 0.05	34.8 ± 1.9
1-Heptene	18.6 ± 0.30	23.7 ± 2.0	4.02 ± 0.01	35.0 ± 1.3
1-Octene	35.4 ± 0.90	29.1 ± 3.9	10.7 ± 0.05	38.8 ± 2.2
1-Nonene	73.3 ± 2.40	39.5 ± 5.7	27.6 ± 0.12	42.3 ± 2.2
Benzene	237. ± 0.83	29.3 ± 1.2	2.61 ± 0.04	30.3 ± 2.6
Toluene	455. ± 1.95	32.4 ± 1.2	7.86 ± 0.10	36.4 ± 2.3
Ethylbenzene	746. ± 4.92	34.5 ± 1.8	20.2 ± 0.26	40.4 ± 2.9
m-Xylene	875. ± 6.23	35.5 ± 2.1	22.7 ± 0.32	40.9 ± 3.4
p-Xylene	829. ± 5.25	35.3 ± 2.0	22.1 ± 0.27	41.2 ± 3.1

Chromatographic packings were prepared by coating 3MS on Chromosorb P AW 60/80 (Johns-Manville pink diatomaceous earth support) in a rotary evaporator, under a nitrogen stream and gentle heating, using chloroform as the volatile solvent. Six different packings, containing 5.11_3, 7.02_6, 9.05_1, 11.53_8, 15.74_6 and 19.51_0 % by weight of 3MS were prepared. Coated supports were packed into 0.53 cm I.D. stainless steel tubes, 0.50 or 1.0 m in length.

Column temperature was controlled to better than ±0.05°C by immersion in a water bath. Nitrogen was used as carrier gas; it was successively passed through a molecular sieves trap (Davidson 5A), a Brooks 8606 pressure regulator, a Brooks 8743 flow controller and a 2 m x 1/8 in O.D. coiled copper tube immersed in the column bath. Inlet pressures were measured with a mercury manometer at a point between the copper coil and a Swagelock 1/4 in s.s. "T"; one branch of the latter was provided with a septum through which solute vapors were injected by means of Hamilton microsyringes; the column was connected to the remaining branch. Detection was performed with a Hewlett-Packard 5750 FID and electrometer whose signals were fed to a Hewlett-Packard 3396A integrator.

Sample sizes were of the smallest size compatible with instrumental noise (about 10 nmol); solute vapors and a small methane sample were simultaneously injected, and adjusted retention times were measured to 10^{-3} min between the maxima of the solute and the methane peaks. Specific retention volumes (V_g^o) and net retention volumes per gram of packing (V_N^o) were calculated in the usual form [9] from adjusted retention times and values of the experimental variables.

RESULTS AND DISCUSSION

Specific retention volumes measured in a given column were fitted to the equation

$$\ln V_g^o = -\Delta H_S^o / RT + \text{constant} \qquad (1)$$

where ΔH_S^o, the heat of sorption, may signify different things depending on the retention mechanism(s). Differences between V_g^o values calculated by means of Eq. (1) and experimental values were smaller than 0.3%; interpolation was thus very accurate and data obtained in different columns at slightly different temperatures could be corrected to a common temperature to enable further elaboration of results. Within experimental error (between ± 1% and ± 4% at a 95% confidence level) the heats of sorption were found to be independent of stationary phase loading.

In Figure 1 V_N^o values at 43°C for a group of selected hydrocarbons, representative of different families, have been plotted against the percentage by weight of 3MS in the packing, w. There are notorious differences between the solutes and in none of the cases the retention can be explained exclusively in terms of solution in the stationary phase, since straight lines through the origin should be expected in that case; the existence of more than one retention mechanism is made evident. Conder *et al.* [5] proposed a model that takes realistically into account the most important possible contributions to solute retention; their model may be summarized in the equation

$$V_N^o = K_L V_L + K_A A_L + K_S A_S \qquad (2)$$

where K_L is the liquid-gas partition coefficient, K_A and K_S are the adsorption coefficients at the gas-liquid and at the liquid-solid interfaces, respectively, and V_L, A_L and A_S represent the stationary phase volume, the gas-liquid interfacial area and the solid-liquid interfacial area, all of them expressed per gram of packing. Adsorption on uncovered portions of the solid support, not included in Eq. (2), needs not to be considered when more than 2-3% by weight of a polar stationary phase is coated on the polar surface of Chromosorb P, whose specific surface area is about 4 m^2g^{-1}. Furthermore, it is highly improbable that 3MS molecules, highly polar and in enormous excess, might be displaced from their positions on the solid surface by hydrocarbon molecules. These considerations indicate that for the systems and experimental conditions of this work K_L and K_A can be evaluated by fitting V_N^o to Eq. (2) with $K_S = 0$.

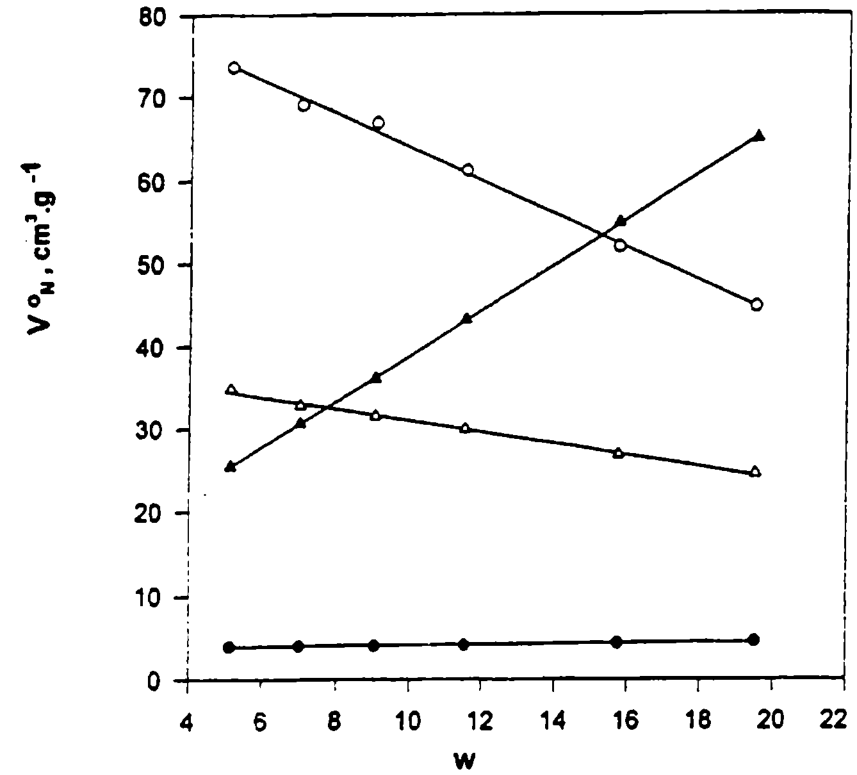

Fig. 1.- Retention volume per gram of packing at 43 °C, V_N^o, against percentage by weight of 3MS in the packing, w.
O: n-Decane; Δ: 1-nonene; ●: methylcyclohexane; ▲: toluene.

In order to use the reduced form of Eq. (2) the areas A_L remain to be evaluated; this was done by following the proposal of Martire *et al.* **[10]**, *i.e.* combining statically measured values of K_L and K_A for benzene and cyclohexane in β,β'-thiodipropionitrile (TDPN) with retention volumes obtained for both solutes in columns containing different loadings of TDPN on Chromosorb P and assuming that at the same loading of TDPN or 3MS calculated on a per volume basis both liquids have equal exposed surface areas. Thus obtained surface areas drop almost lineally with w for packings containing more than about 4 mL of stationary phase per 100 g of packing; this is why the plots of V_N^o against w are straight lines with negative slopes for solutes whose retention is strongly adsorption dominated, as normal decane (see Figure 1).

Calculations performed by the same authors **[10]** indicate that the apparent liquid film thickness on Chromosorb P when w = 5% is about 30nm, and 200 nm when w = 20%. A volume of 1.3×10^{-22} cm^3/molecule can be calculated for 3MS in the liquid state at 40°C. If it is assumed that each molecule moves freely within a spherical cell with diameter d, a value of d = 0.6 nm can be calculated; this means that a stationary phase film 50 molecules thick could be calculated for the more lightly loaded packing in the present work. It is difficult to ascertain if support influence can be felt at the gas-liquid interface of such a film, and what fraction of the liquid is under true bulk conditions. This is an old and unresolved discussion between chromatographers; probably the best answer is given by the results in Figure 1, that shows that V_N° values obtained with the lower loadings fall in line with those measured with the higher ones, for which films of up to 330 molecules can be calculated.

Values of K_L (intercepts) and K_A (slopes) were obtained from the linear regression of V_N° / V_L against A_L / V_L; the equation of 3MS density versus temperature given by Lemire and Sears [1] was employed. Correlation coefficients were always larger than 0.999, and in many cases larger than 0.9999.

Standard enthalpies of solution were computed with the equation

$$\Delta H_L^\circ = -R[\partial \ln K_L / \partial(1/T)] - RT(1-\alpha_1 T) \qquad (3)$$

where α_1 is the thermal expansion coefficient of 3MS, computed by means of the equation of Lemire and Sears. ΔH_L° corresponds to the transfer of one mole of solute from an ideal vapor phase at a pressure of 1 atm to an hypothetical solution where it is at unitary molar fraction with behavior extrapolated from infinite dilution [11]. On applying Eq.(3) a constant enthalpy of solution through the experimental temperature range was assumed, and non-idealities of the vapor phase were neglected. Both assumptions are justified by the unavoidably large errors in the measurement of ΔH_L° by combining data obtained in several columns.

Standard enthalpies of adsorption were calculated by means of the equation

$$\Delta H_A^\circ = R[\partial \ln K_A / \partial(1/T)] \qquad (4)$$

and correspond to the transfer of one mole of solute from the ideal vapor phase at 1 atm to an ideal adsorbed state where adsorbate molecules interact with the surface only [12]. Again, temperature independence of ΔH_A° and an ideal vapor phase was assumed in the calculations.

Solution and adsorption properties for the fifteen hydrocarbons in 3MS at 40°C were gathered in Table 2. Uncertainties given for K_L and for K_A are the standard deviations for the intercepts, σ (K_L), and for the slopes, σ (K_A), respectively, obtained in the regression of V_N° / V_L against A_L/V_L. The confidence ranges for ΔH_L° and ΔH_A° at the 95% level were calculated taking into consideration that two successive regressions are necessary to calculate the enthalpy values [7].

The percent contribution of adsorption to the retention volume for four representative hydrocarbons in the columns containing extreme 3MS loadings, calculated using K_L and K_A values, are given in Table 3. In the first place these results give us an idea of the enormous errors that the neglect of adsorption would introduce in the study of the solution process; in the second, they explain the large errors made on computing ΔH_L° for paraffins. In the case of n-decane, a solute whose percent adsorption retention is 95% at the 5.11_3 % loading and 70%at the 19.51_0% loading, that error amounts to 41% of ΔH_L°

In order to investigate any correlation between solution and adsorption properties values of K_A at 40°C have been plotted against those of K_L in Figure 2. Points corresponding to solutes belonging to a given family fall on a common straight line, but there is not a general correlation involving hydrocarbons of different families. A similar behavior can be detected in the plot of ΔH_A° against ΔH_L° in Figure 3, although the trends are not so clear in this case as a consequence of the large errors involved in the measurement of the enthalpies.

Table 3

Percent contribution of adsorption to the retention volume for extreme loadings at 45°C

SOLUTE	5.11_3 % w/w	19.51_0 % w/w
n-Heptane	91.9	58.3
1-Heptene	87.4	46.1
Methylcyclohexane	56.4	32.4
Toluene	36.7	6.7

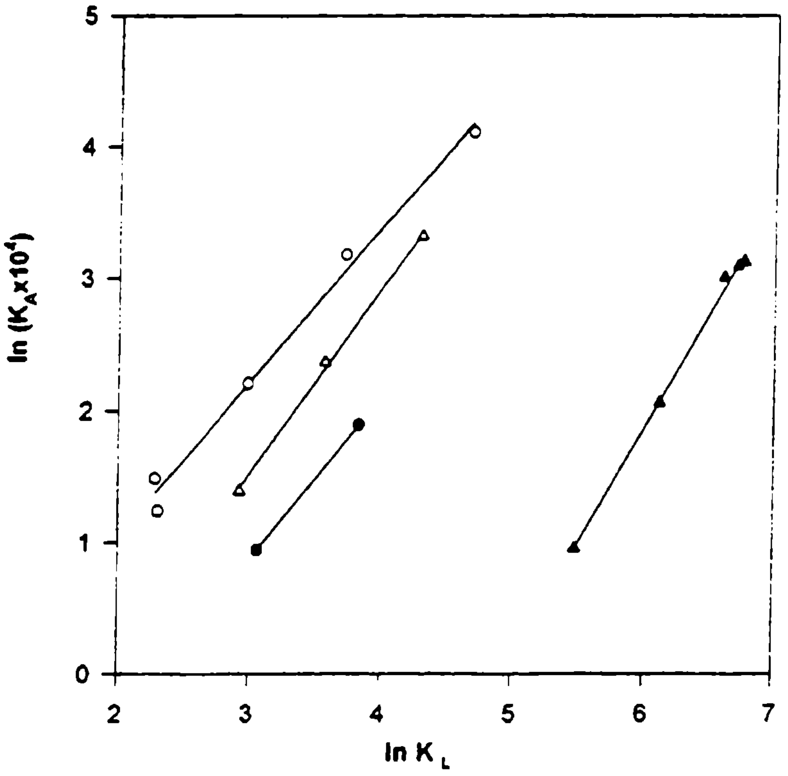

Fig. 2.- Relationship between adsoption and partition coefficients at 40 °C.
O: Alkanes; Δ: 1-alkenes; ●: cycloalkanes; ▲: aromatics.

Bulk phase activity coefficients at infinite dilution, $\gamma_2^{b,\infty}$, were calculated by means of the equation

$$\gamma_2^{b,\infty} = RT / p_2^\circ K_L v_1^\circ \qquad (5)$$

where p_2° is the solute vapor pressure and v_1° the stationary phase molar volume [6]. Results obtained in 3MS at 40°C can be read on Table 4, and compared with the results obtained at 25°C in FA [13] and in EG [14]. The smallest values are obtained when 3MS is the solvent; differences with EG and FA are very important, and cannot be explained by the temperature difference. This trend is in coincidence with the absence of surfactant self-aggregation processes in 3MS found by Evans *et al.* [3]. It is important to stress that if positive deviations from the ideal behavior depend mainly on solute-solvent c.e.d. differences, and if the solvents c.e.d.'s are correctly gauged by the $\sigma/v^{1/3}$ quotients, the values of the activity coefficients in 3MS should be intermediate between those in FA and EG.

Table 4

Bulk liquid and gas-liquid interface activity coefficients of hydrocarbons in polar solvents

	FA, 25°C		EG, 25°C		3MS, 40°C	
SOLUTE	$\gamma_2^{b,\infty}$	$\gamma_2^{s,\infty}$	$\gamma_2^{b,\infty}$	$\gamma_2^{s,\infty}$	$\gamma_2^{b,\infty}$	$\gamma_2^{s,\infty}$
n-Heptane	2220	110	1020	29.6	277	26.7
n-Octane	3880	163	1730	39.2	415	31.1
n-Nonane	6410	230	2850	53.5	585	39.3
n-Decane					650	51.1
2,2,4trimethylpentane	2280	134	1150	32.8	269	29.9
Methylcyclohexane	914	79.1	542	21.5	130	15.7
Ethylcyclohexane	1710	118	773	29.7	199	23.0
1-Heptene	1010	70.4	507	21.6	122	16.6
1-Octene	1850	103	914	28.6	191	21.6
1-Nonene					272	29.0
Benzene	52.3	15.2	32.3	5.64	5.89	2.49
Toluene	102	22.0	61.7	7.90	9.48	3.50
Ethylbenzene	196	32.0	112	10.3	15.9	4.63
m-Xylene	214	33.6	124	11.2	15.4	4.88
p-Xylene	208	33.9	123	11.2	15.5	4.98

Surface activity coefficients at infinite dilution, $\gamma_2^{s,\infty}$, were calculated with the equation deduced by Eon and Guiochon [15] for a monolayer model:

$$\gamma_2^{s,\infty} = [RT / p_2^{o}(K_L v_1^{o} + K_A a_1^{o})] \exp[a_2^{o}(\sigma_1^{o} - \sigma_2^{o}) / RT] \qquad (6)$$

where σ_1^o and σ_2^o represent the stationary phase and the solute surface tensions in the pure state, respectively; a_1^o and a_2^o are the corresponding molar surface areas, approximated by the relation $a_i^o = 1.2N^{1/3}(v_i^o)^{2/3}$, where N is Avogadro's constant. This last is a rough approximation, only valid for spherical molecules; a more exact calculation would demand to take into account not only the molecular shape but also to know how the molecule settles on the surface. The results obtained for adsorption on 3MS at 40°C have been gathered in Table 4, together with the results taken from former papers for FA and EG at 25°C [16].

In contrast to the trends observed in Figure 2, points corresponding to hydrocarbons of different families fall on a common straight line in Figure 4, where logarithms of activity coefficients in the surface phase are plotted against the corresponding values in the bulk phase; the correlation coefficient is 0.997, and a similar behavior is observed for the results in FA and in EG [16]. For systems with strong adsorption $K_A a_1^o \gg K_L v_1^o$, and from Eq. (5) and Eq. (6)

$$K_A / K_L \cong (\gamma_2^{b,\infty} v_1^{o} / \gamma_2^{s,\infty} a_1^{o}) \exp[a_2^{o}(\sigma_2^{o} - \sigma_1^{o}) / RT] \qquad (7)$$

that indicates that the different trends displayed in both figures can be attributed to the very unlike surface tensions exhibited by hydrocarbons of different families in the pure state.

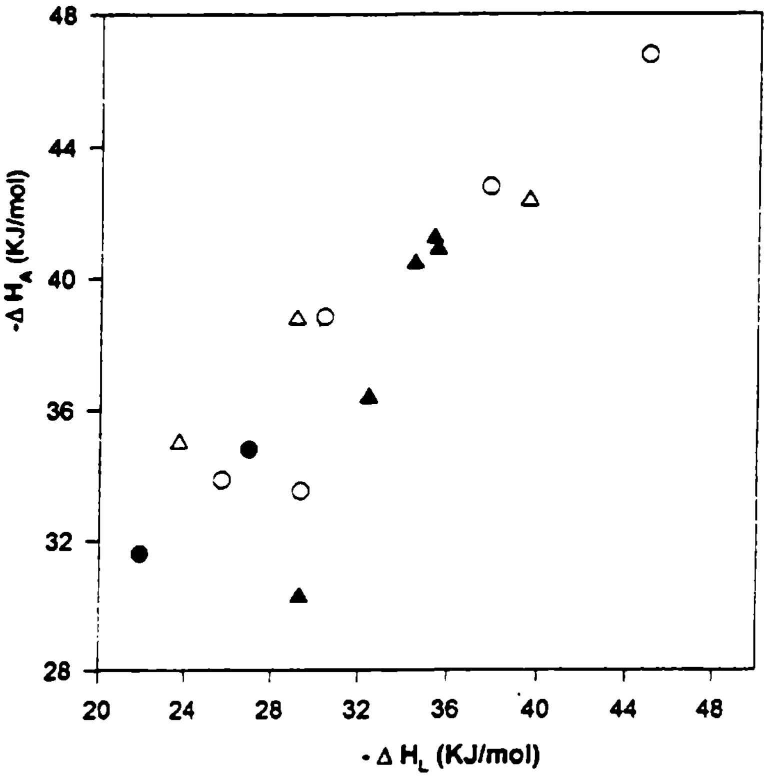

Fig. 3.- Relationship between adsorption and partition enthalpies. Symbols as in Figure 2.

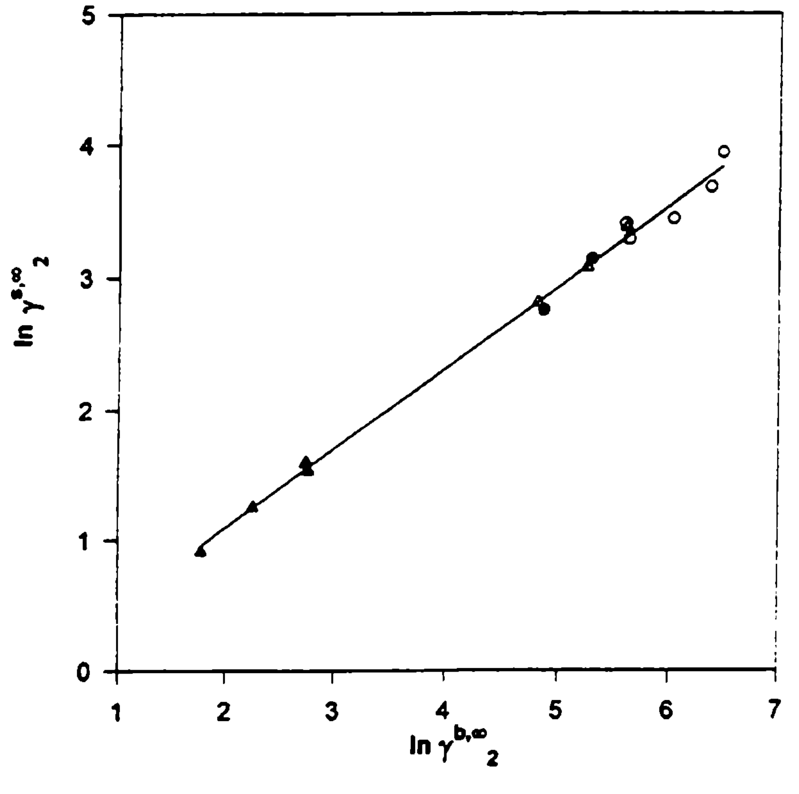

Fig. 4.- Relationship between gas-liquid interface and bulk liquid infinite dilution activity coefficients at 40°C. Symbols as in Figure 2.

For all the studied systems surface activity coefficients are smaller than their bulk counterparts. This is the trend that could be expected: since the number of nearest neighbors is smaller at the surface than in bulk solution, nonideality effects are expected to be lower at the surface. However when the values obtained in both phases of the three solvents are compared it can be seen that the activity coefficients on the 3MS surface are larger than what could be predicted on the basis of the values of the activity coefficients in the bulk phase; alkanes surface activity coefficients in 3MS, for instance, are almost equal to those in EG, in spite of very large differences between the bulk activity coefficients in both solvents. These trends are made evident in Figure 5, where the quotients ($\gamma_2^{s,\infty} / \gamma_2^{b,\infty}$) in 3MS have been plotted against the corresponding quotients in FA or EG.

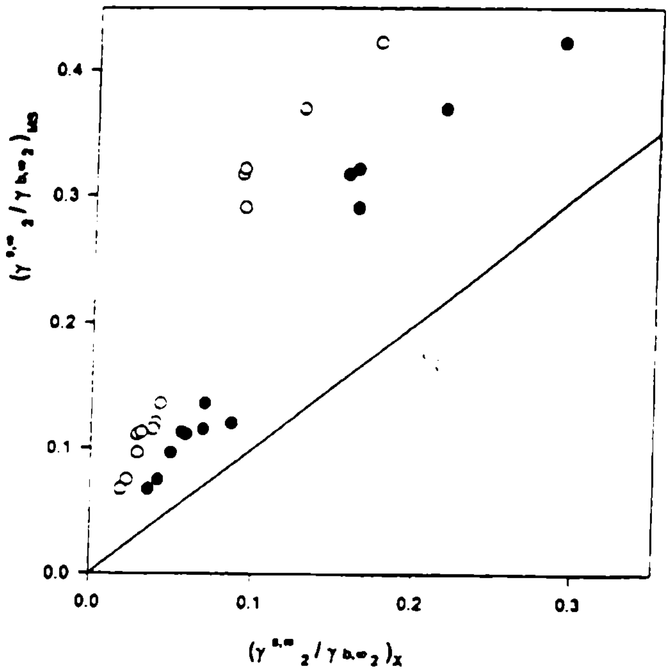

Fig. 5.- Relationship between the quotients ($\gamma_2^{s,\infty} / \gamma_2^{b,\infty}$) in 3MS and in the stationary phase X. o: X = EG; o: X = FA. The line corresponds to equal values in both stationary phases.

This figure tells us that the relationship between surface and bulk properties can be very different for different solvents, and about the unpredictability of surface properties exclusively on the basis of bulk properties and vice versa. This may be attributed to structural rearrangements of solvent molecules at the surface, through processes that can be very different in a given solvent than in another. From this point of view, the surface tension of 3MS can be the result of an intense dipoles orientation process at the liquid surface, that keeps very little relation with the random distribution in the bulk suggested by the value of its *g* factor.

In order to further test this possibility the dispersion contributions to the surface tension, σ_1^d, of FA, EG and 3MS were calculated by two methods:

I. The proposal of Hauxwell and Ottewill **[17]**, as applied by Hartkopf **[18]** to gas chromatographic data: a plot of $K_A p_2^\circ$ against σ_2° for saturated hydrocarbons (alkanes or cycloalkanes) results in a straight line that intersects the abscissa at $\sigma = \sigma_1^d$.

II. By Dorris and Gray proposal (19), according to which

$$\sigma_1^d = (\Delta G_{CH_2} / 2\,N\,a_{CH_2})^{1/2} \sigma_{CH_2}^{-1} \tag{8}$$

where N is Avogadro number, a_{CH_2} is the cross-sectional area of -CH$_2$- groups (0.06 nm^2), σ_{CH_2} is the surface free energy of a surface made up of only -CH$_2$- groups (35 dyn/cm, as calculated for poly(ethylene)), and ΔG_{CH_2} is given by

$$\Delta G_{CH_2} = RT \ln(K_{A,n+1} / K_{A,n}) \tag{9}$$

where $K_{A,n+1}$ and $K_{A,n}$ are the adsorption coefficients for normal alkanes with n+1 and n carbon atoms, respectively. The results have been gathered in Table 5, that shows that both methods are only in a moderate agreement. Both methods indicate important polar contributions, σ_1^h, to the surface tension of 3MS (as calculated by the difference $\sigma_1^h = \sigma_1^o - \sigma_1^d$), not very different from those corresponding to FA and EG.

Table 5

Dispersion contributions to the surface tension of solvents calculated by two different methods

SOLVENT	METHOD I[a]	METHOD II[b]
FA	29.6	28.8
EG	30.2	28.6
3MS	28.3	32.0

Units: dyn/cm

[a] Ref. 17 and 18. [b] Ref. 19

These results reflect important differences between the surface (as given by σ_1^h) and the bulk (according to its Kirkwood g factor) properties of 3MS. Under these circumstances the prediction of its c.e.d. through the quotient $\sigma/v^{1/3}$ can result in a serious overestimation, and this can be the origin of its incapacity for forming micelles and of the relatively small positive deviations from Raoult's law displayed by hydrocarbons.

ACKNOWLEDGEMENTS

This work was sponsored by CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas de la Rep. Argentina) and by CICPBA (Comisión de Investigaciones Científicas de la Prov. de Buenos Aires).

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