

CHROM. 12,921

GAS CHROMATOGRAPHIC STUDY OF SOLUTION AND ADSORPTION OF HYDROCARBONS ON GLYCOLS

I. DIETHYLENE GLYCOL AND TRIETHYLENE GLYCOL

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(First received March 18th, 1980; revised manuscript received April 29th, 1980)

SUMMARY

Interfacial adsorption is shown to influence the gas chromatographic retention behaviour of hydrocarbons when using glycols as stationary phases. This interfacial effect can be neglected only for lower aromatic hydrocarbons, as demonstrated by the determination of partition and interfacial adsorption coefficients.

Activity coefficients at infinite dilution were calculated; they compare favourably with those determined statically when using the method proposed by Martire *et al.* for the evaluation of exposed areas, whereas the use of experimental values given by Serpinet *et al.* led to erratic results.

Solution and adsorption thermodynamic characteristics of the systems studied are briefly discussed.

INTRODUCTION

Gas chromatography has been used successfully in the determination of thermodynamic parameters of solution, especially when dealing with non-electrolytes, and very precise results are obtained whenever a single retention mechanism occurs. Much work has been published, particularly on infinitely dilute systems^{1,2}.

The gas chromatographic study of solutions may be complicated by solute adsorption at the gas-liquid interface^{3,4}. As the stationary phase is dispersed on a porous solid, the ratio between the interfacial area and liquid volume is large, thus facilitating adsorption processes, especially in systems exhibiting large positive deviations from Raoult's law, where the solute tends to be expelled from the bulk of the solvent towards its surface, basically because solvent-solvent interactions are much more intense than those between solute and solvent molecules.

Mixed processes, involving both dissolution and adsorption, might be expected to govern chromatographic retention in systems constituted by hydrocarbons and highly polar stationary phases; as highly active sites at the surface of the solid

support are blocked by solvent molecules, it is improbable that adsorption of the hydrocarbon might occur on such a surface.

Under these circumstances, the net retention volume per gram of packing, V_N^0 , is expressed by the equation proposed by Martin³:

$$V_N^0 = K_L V_L + K_A A_L \quad (1)$$

where K_L is the partition coefficient, equal to the limiting slope in the graph of concentration in the stationary phase vs. concentration in the vapour phase when the latter tends to zero, K_A is the adsorption coefficient at the gas-liquid interface, equal to the ratio between the solute concentration in excess at the surface as compared with the bulk concentration in the liquid and the concentration in the gaseous phase, V_L is the volume of the stationary liquid phase per gram of packing and A_L is the exposed surface area of same liquid per gram of packing.

Physico-chemical measurements by means of chromatographic techniques are of special interest in extraction processes on an industrial scale. Thus, the separations of aromatic hydrocarbons from oil fractions in which they are mixed with paraffinic and naphthenic hydrocarbons are conducted with high-polarity solvents, leading to the formation of strongly non-ideal solutions. The study of these systems and the further design of extraction operations are intimately related to activity coefficients at infinite dilution.

When evaluating the selectivity of a given solvent, the limiting separation factor parameter, $\beta_{S/A}^\infty$, is used, this being defined as $\beta_{S/A}^\infty = \gamma_S^\infty / \gamma_A^\infty$, where γ_A^∞ and γ_S^∞ are the activity coefficients of an aromatic and a saturated hydrocarbon, respectively, both at infinite dilution, in the solvent. The greater the value of $\beta_{A/S}^\infty$, the more selective the solvent will be.

For solutions with highly positive deviations from ideal behaviour, the solvent capacity towards aromatic hydrocarbons might be approximated by $X_A = 1/\gamma_A^\infty$, where X_A is the molar fraction.

In this work we studied the nature of the phenomena that control the chromatographic behaviour of hydrocarbons within columns containing a glycol (diethylene or triethylene glycol) as the stationary phase, and tried to quantify the individual contributions ascribable to solution and to adsorption at the gas-liquid interface, so as to be able to correct, when necessary, the retention parameters, particularly activity coefficients at infinite dilution, already available in the literature⁵.

The use of values for surface areas determined experimentally elsewhere⁶ on comparable systems is matched with the reasoning developed and proposed by Martire *et al.*⁷ for the calculation of thermodynamic functions of solution and of adsorption on the gas-glycol interface.

EXPERIMENTAL

Apparatus

The equipment used was as described earlier⁸. Columns were thermostated to within 0.05°C by immersion in a modified Lauda U3 bath. Analytical-grade nitrogen, previously purified by passing through a trap charged with 5A molecular sieve, was used as the carrier gas. A Model 8743 Brooks regulator made it possible to control the

flow. In spite of the low vapour pressures of diethylene and triethylene glycol within the experimental temperature range, a 50 cm \times $\frac{1}{4}$ in. I.D. pre-column, packed with a filling containing the highest percentage of stationary phase used and submerged in the same bath as the analytical column, was inserted between the flow regulator and the injector⁸ so as to keep carrier gas saturated with stationary phase, thus ensuring stability of the packing.

Columns were built from 1/4-in. O.D. stainless-steel tubing, with a length of 25 cm when handling aromatic hydrocarbons and 100 cm for the remaining hydrocarbons. The carrier gas flow-rate was measured by means of a bubble flow meter at the exit of the detector (Hewlett-Packard Model 5750 flame-ionization detector); the exit pressure was always room pressure, and was measured every 2 h.

Columns and reagents

The solvents (stationary phases) used were diethylene glycol (Carlo Erba, Milan, Italy; chromatographic grade) and triethylene glycol (Merck, Darmstadt, G.F.R.; for synthesis purposes), both distilled at reduced pressure under nitrogen and percolated through a column packed with 4A molecular sieve, in an attempt to exclude water as far as possible; Karl Fischer determinations showed that the final products contained, in both instances, less than 0.10% of water. The purity of the solvents was checked by chromatography at 180°C, using a 180 cm \times 1/8 in. O.D. stainless-steel column with 4% SE-30 as the stationary phase on 80–100-mesh Chromosorb W.

Acid-washed (with a mixture of concentrated hydrochloric and nitric acids) 60–80-mesh Chromosorb P was used as the solid support. Packings were prepared by carefully weighing both the solid support and the stationary phase in a tightly closed

TABLE I
COLUMN CHARACTERISTICS AT 25°C

Stationary phase	Parameter*	Percentage							
		24.70	19.70	14.73	11.97	9.696	5.778	5.095	
Diethylene glycol	W_1	2.3863	2.1328	1.8529	—	1.8272	1.7040	—	
	W_2	9.3426	8.4275	8.0258	7.8130	—	—	7.4524	
	V_L	0.2220	0.1771	0.1324	0.1076	0.0871	0.0519	0.0458	
	$A_L(1)$	0.281	0.504	0.744	0.883	1.01	1.26	1.31	
	$A_L(2)$	0.95	1.15	1.43	1.62	1.81	2.22	2.32	
		Percentage							
		24.44	23.94	19.81	18.97	14.55	9.396	9.088	4.651
Triethylene glycol	W_1	2.1286	—	2.0659	—	1.9910	—	1.6620	1.6262
	W_2	—	9.2990	—	8.5296	8.4145	7.8778	—	7.2742
	V_L	0.2183	0.2138	0.1769	0.1694	0.1300	0.0839	0.0812	0.0415
	$A_L(1)$	0.291	0.315	0.504	0.543	0.747	1.04	1.05	1.34
	$A_L(2)$	0.97	0.98	1.15	1.18	1.45	1.83	1.85	2.37

* W_1 = grams of packing in a 25-cm column; W_2 = grams of packing in a 100-cm column; V_L = volume of liquid stationary phase at 25°C per gram of packing; $A_L(1)$ = area of liquid stationary phase per gram of packing (m^2/g), calculated according to Martire *et al.*⁷; $A_L(2)$ = area of liquid stationary phase per gram of packing (m^2/g), using experimental data from Serpinet *et al.*⁶.

flask, avoiding unnecessary exposure to the atmosphere; the flask was subsequently rotated for 10 h at approximately 50 rpm. The stationary phase to solid support ratios and other column characteristics are given in Table I.

The purity of each hydrocarbon used was greater than 99%; as the solute purity is not a critical factor in this kind of study, they were used without further purification. Twenty-one hydrocarbons of different types were studied (Table II).

Procedure

Hydrocarbons were injected with a 10- or a 50- μ l Hamilton syringe, applying the headspace sampling technique. In each instance the sample size was the smallest compatible with the detector noise level. Every solute gave symmetric peaks, thus proving that, whatever the retention mechanism, runs have been conducted within the concentration range for which Henry's law is obeyed.

The hydrocarbons were always injected individually, together with a small amount of methane. Adjusted retention times were measured on the chart between the methane peak and the solute peak maximum. Calculations were made based on three individual values of the retention time for each set of solute, column and temperature. Carrier gas flow-rates were kept between 15 and 80 cm^3/min , so as to obtain reasonable retention times. The columns were operated at four different temperatures within the range 20–31°C.

RESULTS

Graphs of net retention volume per gram of packing *versus* stationary phase percentage are shown in Fig. 1 for some representative hydrocarbons in both solvents. It can be seen that the retention behaviour of none of the systems except benzene could be explained by a single mechanism, as otherwise each pair of straight lines would converge at the origin.

Considering the evidence for mixed processes, the most probable sorption mechanisms are (1) dissolution in the stationary phase, (2) adsorption at the gas-liquid interface, and (3) adsorption on the solid support. The last of these mechanisms would occur either through direct adsorption of solute molecules on bare active sites on the support or through displacement of glycol molecules from some of the active sites. Both processes are highly improbable because, on the one hand, the least percentage of stationary phase used (4.651%) largely exceeds the amount required for a monolayer to be formed and, on the other, in addition to the fact that the amounts of both stationary phases are considerably greater than the small amount of solute, the polarity of the glycol molecules makes it very unlikely that they are replaced from the acidic sites on the surface of the support by hydrocarbon molecules. These arguments are supported by other studies⁹⁻¹¹.

Further study of the behaviour of solutes in solution and on the gas-liquid interface making use of eqn. 1 requires a knowledge of the exposed areas of stationary liquid.

These areas have been calculated using two different approaches: firstly, and on the basis of the already established^{6,12,13} fact that the exposed area does not depend on the nature but on the volume of the stationary (liquid) phase, they have been estimated by interpolation and extrapolation between and beyond values measured

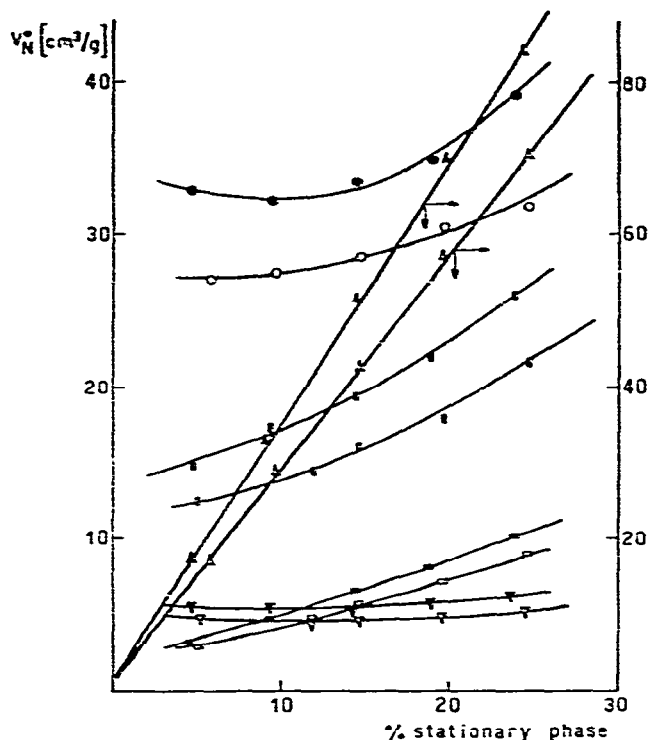


Fig. 1. Representative net retention volumes per gram of column packing as a function of stationary phase percentage: \circ , \bullet , *n*-nonane; \triangle , \blacktriangle , benzene; \square , \blacksquare , 1-octene; \square , \blacksquare , cyclohexane; ∇ , \blacktriangledown , 2,2,4-trimethylpentane. Open symbols, diethylene glycol; closed symbols, triethylene glycol.

directly⁶ for different percentages of glycerol used as the stationary phase on Chromosorb P.

Secondly, they were calculated following Martire *et al.*'s proposal⁷, making use of the K_L and K_A values they determined for cyclohexane on thiodipropionitrile in a tightly closed chamber containing a McBain balance and a Du Nouy tensiometer to compare chromatographic data with static values, and retention volumes obtained by Martin³ for this system, assuming that for the same stationary phase to Chromosorb P ratio both glycols and thiodipropionitrile exhibit the same exposed surface area, an assumption validated by the coincidence of the surface area values obtained when they are measured for two different liquids on the same support^{3,14}.

The values thus obtained are given in Table I. Stationary phase volumes were calculated by using density data at different temperatures compiled by Riddic and Bunger¹⁵.

Net retention volumes (V_N) were calculated from the adjusted retention times and operating conditions in the usual way¹⁶. V_N data for each column were adjusted to the following equation:

$$\log V_N = -\Delta H/2.3 RT + \text{constant}$$

where ΔH is the enthalpy of sorption calculated by the least-squares method.

Experimental values of V_N differ from those calculated by interpolation by at most 1%, the differences being 0.5% or less in most instances.

K_L values were obtained by determining (using the least-squares method) the slopes of the lines resulting from plotting V_N^0/A_L vs. V_L/A_L ; analogously, K_A values were calculated by the same technique from the slopes of the V_N^0/V_L vs. A_L/V_L graphs.

The values obtained are given in Tables II and III, together with the 95% confidence intervals obtained from the standard deviations of the slopes and t factors. K_L values obtained for benzene and toluene in both stationary phases from experimental data, when $K_A = 0$ in eqn. 1, fall within the experimental error for K_L calculated by use of the complete equation. In contrast, and as would be expected because of the rare incidence of adsorption processes, the deviation of the K_A values obtained for both solutes is large.

TABLE II
PARTITION AND ACTIVITY COEFFICIENTS AT 25°C

Solute	Diethylene glycol		Triethylene glycol	
	K_L	γ_2^∞	K_L	γ_2^∞
<i>n</i> -Hexane	11.7 ± 0.7	110	13.7 ± 0.4	67.0
<i>n</i> -Heptane	25.7 ± 1.4	166	30.8 ± 1.1	98.5
<i>n</i> -Octane	55.7 ± 3.4	250	69.3 ± 3.9	143
<i>n</i> -Nonane	122 ± 2	372	155 ± 9	208
Cyclohexane	39.1 ± 1.5	50.9	45.9 ± 1.2	30.8
Methylcyclohexane	53.5 ± 2.4	79.2	64.4 ± 2.4	46.8
Ethylcyclohexane	128 ± 6	117	159 ± 7	67.1
Cyclohexene	84.3 ± 3.0	26.0	100 ± 3	15.6
<i>cis</i> -2-Hexene	25.5 ± 0.3	50.6	29.8 ± 0.8	30.8
1-Heptene	41.7 ± 2.1	83.5	50.0 ± 1.8	49.5
1-Octene	89.3 ± 5.0	128	110 ± 5	74.1
2,2,4-Trimethylpentane (isooctane)	20.8 ± 1.4	195	24.2 ± 1.0	117
2,4,4-Trimethyl-1-pentene (isooctene)	43.6 ± 2.2	109	52.1 ± 2.1	64.7
Benzene	216 ± 2	6.48	383 ± 6	3.80
Toluene	656 ± 2	10.4	809 ± 10	6.01
Ethylbenzene	1250 ± 2	16.2	1551 ± 15	9.31
<i>n</i> -Propylbenzene	2213 ± 9	25.9	2816 ± 17	14.5
Isopropylbenzene	1740 ± 15	24.3	2193 ± 18	13.7
<i>o</i> -Xylene	1899 ± 10	15.5	2418 ± 22	8.68
<i>m</i> -Xylene	1337 ± 3	17.6	1689 ± 19	9.89
<i>p</i> -Xylene	1280 ± 4	17.5	1617 ± 19	9.85

Activity coefficients at infinite dilution, γ_2^∞ , were calculated from the usual expression $\gamma_2^\infty = RT/p_2^0 K_L v_1^0$, where v_1^0 is the molar volume of the solvent and p_2^0 the saturation pressure of pure solute at temperature T (°K). Vapour pressures at each temperature were calculated making use of the constants for the Antoine equation compiled by Riddic and Bunger¹⁵. No corrections were introduced because of non-ideality in the vapour phase, as it was found to be negligible because positive and negative terms cancelled out.

TABLE III
THERMODYNAMIC FUNCTIONS OF ADSORPTION AT 25°C

Solute	Diethylene glycol			Triethylene glycol		
	$K_A \cdot 10^5$ (cm)	$-\Delta H_A^0$ (kcal/mole)	$-\Delta S_A^0$ (e.u.)	$K_A \cdot 10^5$ (cm)	$-\Delta H_A^0$ (kcal/mole)	$-\Delta S_A^0$ (e.u.)
<i>n</i> -Hexane	8.85 ± 0.54	7.3	9.9	9.84 ± 0.24	6.6	7.4
<i>n</i> -Heptane	23.4 ± 1.2	8.2	11.1	26.9 ± 0.7	7.7	9.1
<i>n</i> -Octane	62.4 ± 3.0	9.8	14.4	74.0 ± 2.8	9.6	13.6
<i>n</i> -Nonane	164 ± 3	10.3	14.1	199 ± 8	10.7	15.3
Cyclohexane	8.03 ± 1.75	7.3	10.1	8.62 ± 0.67	6.6	7.8
Methylcyclohexane	18.2 ± 2.0	8.1	11.2	20.6 ± 1.9	8.0	10.5
Ethylcyclohexane	48.0 ± 5.6	9.3	13.4	56.0 ± 5.2	9.6	14.0
Cyclohexene	9.19 ± 2.65	8.3	13.3	9.78 ± 2.42	7.6	10.9
<i>cis</i> -2-Hexene	9.76 ± 0.75	6.7	7.7	11.1 ± 0.5	7.0	8.6
1-Heptene	24.8 ± 1.8	8.5	12.1	28.4 ± 1.5	8.2	10.8
1-Octene	65.6 ± 4.6	9.7	14.2	77.5 ± 3.9	9.8	14.0
Isooctane	28.6 ± 1.1	8.2	10.8	33.0 ± 0.7	7.7	8.7
Isooctene	34.7 ± 1.9	8.5	11.2	40.4 ± 1.6	8.6	11.5
Benzene	10.1 ± 2.4	2.8	5.5	8.58 ± 5.53	5.5	4.0
Toluene	27.7 ± 2.0	7.0	6.8	28.4 ± 10.0	8.7	12.5
Ethylbenzene	73.1 ± 4.2	8.7	10.5	84.2 ± 15.3	9.2	12.0
<i>n</i> -Propylbenzene	210 ± 10	10.3	13.8	241 ± 20	10.1	12.9
Isopropylbenzene	172 ± 12	10.5	14.9	201 ± 17	9.7	11.7
<i>o</i> -Xylene	83.7 ± 8.7	10.3	15.6	86.8 ± 18.6	8.0	8.0
<i>m</i> -Xylene	80.3 ± 2.5	9.5	12.9	89.1 ± 15.5	9.0	11.0
<i>p</i> -Xylene	79.0 ± 7.5	9.4	12.7	88.1 ± 15.7	9.0	11.1

Enthalpies of solution, ΔH_S^0 , were calculated from the slopes of the $\ln K_L$ vs. $1/T$ graphs; a correction term, $RT(1 - \eta T)$, was subtracted, where η is the coefficient of thermal expansion of the stationary phase. As Meyer¹⁷ has proved, the enthalpies thus corrected correspond to the transference of 1 mole of solute from an ideal vapour phase at 1 atm to a hypothetical solution at 1 molar fraction but obeying Henry's law. Solute molecules under these conditions are exclusively exposed to interactions with solvent molecules; if one wishes to compare the strength of these interactions with those among solute molecules (solute-solute), the enthalpies of solution obtained should be compared with the enthalpies of condensation, ΔH_L^0 , to a pure liquid from an ideal vapour at 1 atm. The difference $\Delta H_S^0 - \Delta H_L^0$ gives the excess partial molar enthalpy of solution and corresponds to the energy change for 1 mole of solute when passing from a pure real liquid to a hypothetical liquid, or from an infinitely dilute ideal solution to an infinitely dilute real solution. The correction terms $RT(1 - \eta T)$ obtained from density data compiled by Riddic and Bunger¹⁵ for diethylene and triethylene glycol at 25°C were 473 and 469 cal/mole, respectively.

Standard molar free energies of adsorption were calculated from the equation

$$-\Delta G_A^0 = RT \ln (p^0/\pi^0) K_A \quad (2)$$

where p^0 is the pressure in the gaseous reference state and π^0 is the surface pressure in the adsorbed standard state. Following Kemball and Rideal¹⁸, a solute vapour behaving ideally at unit pressure (1 atm) was chosen as the standard gaseous state, and a surface film at a surface pressure of 0.0608 dyne/cm as the adsorbed standard state; this value was deduced by assuming a thickness of 6 Å for the surface layer, this being arrived at by calculating a two-dimensional pressure equivalent to a three-dimensional pressure of 1 atm²⁶. Under these circumstances, $p^0/\pi^0 = 1.67 \cdot 10^7$ l/cm.

By applying the Gibbs–Helmholtz ratio to eqn. 2, it can easily be shown that the enthalpy of adsorption, ΔH_A^0 , can be obtained from the graph of $\ln K_A$ vs. $1/T$. Adsorption functions are given in Table III.

The precisions of enthalpies of adsorption and solution were estimated as described by Castells¹⁹; they depend on the relative importance of the retention mechanism. Thus, for aromatic hydrocarbons, for which a solution mechanism prevails, enthalpies of solution attain the same precision as enthalpies of sorption, *i.e.*, ± 450 cal/mole for triethylene glycol and ± 300 cal/mole for diethylene glycol, but the uncertainty in the measurement of enthalpies of adsorption is much greater, because of the minor occurrence of this process and its consequent small contribution to the experimental chromatographic parameters. In contrast, for solutes for which adsorption is the dominant mechanism (alkanes), the precision of the enthalpies of adsorption is of the same order as that of enthalpies of sorption, while that of solution is smaller, even though the uncertainty is less than twice that for enthalpies of sorption.

DISCUSSION

The K_L and K_A values listed in Tables II and III were obtained by using areas calculated according to Martire *et al.*⁷. The few experimental data that we were able to take from Serpinet *et al.*⁶ lead to highly erratic results and, when the values thus obtained are compared with those from static phase equilibria given in the literature²⁰, large deviations occur with systems for which surface effects are meaningful.

Calculated activity coefficients at infinite dilution, as given in Table II, show a mean deviation of 10% relative to data from phase equilibria²⁰. Experimental values obtained by chromatography⁵, without taking into account surface effects, exhibit mean deviations of about 25% as compared with the same data.

Values of γ^∞ obtained in this work for *n*-alkanes in diethylene glycol were compared with those calculated making use of correlations given by Pierotti *et al.*²¹ at 25°C; the mean deviations were less than 2%. The same deviation was found when our value for the activity coefficient at infinite dilution of benzene in diethylene glycol, extrapolated to 50°C, was compared, with that obtained chromatographically²²; this agreement further validates the extrapolation, especially when the negligible effect of adsorption in this system is taken into account.

Each of the hydrocarbons studied showed a positive deviation from Raoult's law in both solvents; as would be expected, the largest deviations pertain to alkanes and the smallest to aromatic hydrocarbons, olefins and cycloalkanes showing intermediate behaviour. Within each type of hydrocarbon, the deviations increase as the number of carbon atoms increases, whereas they are inversely proportional to the molecular weight of the solvent.

Both glycols are associated liquids, so that it is evident that the dissolution of a given hydrocarbon in such a medium will be the more difficult the higher its molecular volume, owing to the larger number of intermolecular bonds that should be dissociated to provide sufficient room for the guest molecule. On the other hand, as both solvents are highly polar, they must be capable of polarizing delocalized electrons in other molecules, so that energetic interactions in solution will be the more intense the more polarizable is the solute. These criteria agree with the trends found when the hydrocarbons studied are compared. Mean deviations of the $\ln \gamma^\infty$ value in both glycols of only 4% for aliphatic hydrocarbons and up to 10% for aromatic hydrocarbons are found between present experimental values and those obtained by applying the Scatchard-Hildebrand theory²³ for regular solutions as modified by Weimer and Prausnitz²⁴ so as to cover systems in which one of the components is polar, making use of the induction energy terms of Helpinstill and Van Winkle²⁵.

From Table IV it can be seen that enthalpies of solution in both solvents for alkanes and cycloalkanes are always lower than the enthalpies of condensation given in the literature¹⁵, giving excess partial molar enthalpies of solution of 1–2 kcal/mole. This difference is small, approaching zero for aromatic hydrocarbons. Even though experimental evidence to explain the results is scanty, it can be postulated that the dissolution of a hydrocarbon in these solvents involves the energetic effect

TABLE IV
ENTHALPIES OF SOLUTION AND CONDENSATION
DEG = Diethylene glycol; TEG = triethylene glycol.

<i>Solute</i>	$-\Delta H_{\text{S}}^{\circ}(\text{DEG})$ (kcal/mole)	$-\Delta H_{\text{S}}^{\circ}(\text{TEG})$ (kcal/mole)	$-\Delta H_{\text{L}}^{\circ}$ (kcal/mole) ¹⁵
<i>n</i> -Hexane	6.3	5.6	7.5
<i>n</i> -Heptane	7.3	6.3	8.7
<i>n</i> -Octane	8.4	7.7	9.9
<i>n</i> -Nonane	9.6	8.9	11.0
Cyclohexane	6.7	6.0	7.9
Methylcyclohexane	7.4	6.7	8.4
Ethylcyclohexane	8.4	7.7	9.7
Cyclohexene	7.5	7.0	7.9
<i>cis</i> -2-Hexene	7.0	6.3	7.5
1-Heptene	7.6	6.9	8.6
1-Octene	8.8	8.0	9.7
Isooctane	7.1	6.3	8.4
Isooctene	7.8	6.5	8.8
Benzene	8.4	8.1	8.1
Toluene	9.2	9.0	9.1
Ethylbenzene	10.1	9.8	10.1
<i>n</i> -Propylbenzene	10.7	10.5	11.0
Isopropylbenzene	10.7	10.5	10.8
<i>o</i> -Xylene	10.4	10.3	10.4
<i>m</i> -Xylene	10.0	9.9	10.2
<i>p</i> -Xylene	10.0	9.9	10.1

necessary to produce a cavity where the solute molecule can lodge, and explain the different behaviour of aromatic hydrocarbons through the strong interactions of hydroxyl groups in the glycol molecule with the electron cloud of the aromatic ring.

Excess entropy values can be evaluated from data in Tables I and IV; all of them are negative, between 1 and 4 e.u. in triethylene glycol and from 4 to 7 e.u. in diethylene glycol, without distinctions for different types of hydrocarbons. The values in triethylene glycol indicate a higher mobility of hydrocarbon molecules as a consequence of the longer paraffinic chain in the glycol, which favours greater solubility of hydrocarbon solutes in this solvent.

Table V gives the limiting separation factor or selectivity for the pairs *n*-hexane-benzene and *n*-octane-benzene, together with the reciprocal of the activity coefficients at infinite dilution for benzene in diethylene and triethylene glycol. It is clear that both solvents are selective, triethylene glycol showing a greater capacity towards benzene. It can be seen, as Weimer and Prausnitz claim²⁴, that solvent selectivity is affected by the molecular size of the hydrocarbon to be separated. Extrapolation to 50°C of values obtained here is also shown in Table V; they keep almost a constant ratio for each pair considered, although the selectivity decreases.

TABLE V

SELECTIVITIES AND CAPACITIES (TOWARDS BENZENE: $X_B = 1/\gamma_B^\infty$)

H = *n*-hexane; O = *n*-octane; B = benzene.

Solvent	Temperature (°C)	Selectivity		Capacity
		$\beta_{H/B}$	$\beta_{O/B}$	
Diethylene glycol	25	17.0	38.6	0.155
	50	13.8	30.4	0.155
Triethylene glycol	25	17.6	37.7	0.263
	50	13.4	27.8	0.263

Table III includes values of the adsorption thermodynamic functions. In spite of their poor precision, it is possible to detect some common trends and features. Enthalpies of adsorption are, in general, smaller than the corresponding enthalpies of liquefaction, indicating that the gas-glycol interface is a low-energy surface.

Kemball and Rideal¹⁸ calculated the entropy variation associated with the transformation of a three-dimensional into a two-dimensional gas; the variation for the hydrocarbons considered here is about -9 to -10 e.u. The values given in Table III, except for a few, are more negative, suggesting that the adsorbed state corresponds to mobile adsorption as defined by Kemball and Rideal for cases where one degree of freedom (that of translation perpendicular to the surface) is lost.

CONCLUSION

It has been demonstrated that for the hydrocarbons considered, under the experimental conditions employed, it is necessary to take into account surface effects when attempting to ascertain the activity coefficients at infinite dilution by chromatography; among the hydrocarbons studied, these effects can be neglected only with benzene and toluene.

In spite of the association of glycol molecules through hydrogen bonds, the modified theory of the solubility parameter enables the γ^∞ values to be evaluated with good precision (mean deviation of $\ln \gamma^\infty = 4\%$ for alkanes and 10% for aromatic hydrocarbons).

The confidence with which thermodynamic functions at the gas-glycol interface can be determined by chromatography is reasonable for alkanes, intermediate for alkenes, cycloalkanes and propylbenzene, and very poor for cycloalkenes and benzene, either unsubstituted or substituted with low-molecular-weight alkyl chains (C_1 and C_2).

Martire *et al.*'s proposal⁷ for the estimation of exposed liquid areas gives much smaller deviations than experimental data from Serpinet *et al.*⁶ when used for evaluating γ^∞ in these systems, after comparing the resulting values with those obtained statically by equilibrating the phases involved.

ACKNOWLEDGEMENTS

E. L. Arancibia is the holder of a graduate fellowship from the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires. We express our gratitude to Dr. R. C. Castells for stimulating discussions and helpful suggestions.

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