ACTIVITY COEFFICIENTS OF HYDROCARBONS AT INFINITE DILUTION IN DI-N-OCTYLTIN DICHLORIDE. COMPARISON WITH RESULTS OBTAINED IN OTHER ALKYLTIN SOLVENTS

MEDICION POR CROMATOGRAFIA GASEOSA DE COEFICIENTES CON ACTIVIDAD DE HIDROCARBUROS A DILUCION INFINITA EN DICLORO DIOCTILESTAÑO. COMPARACION CON RESULTADOS OBTENIDOS EN OTROS SOLVENTES ALQUILESTANNICOS

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SUMMARY

The gas chromatographic method was employed to measure the infinite dilution activity coefficients of twenty-eight hydrocarbons of different types in di-n-octyltin dichloride between 323.15 and 353.15 K, and of seven branched alkanes in tri-n-octyltin chloride between 313.15 and 333.15 K. A comparison is made between the results obtained for all the solutes in both solvents and in tetra-n-octyltin.

Keywords: *Gas-liquid chromatography, di-n-octyltin dichloride, tri-n-octyltin chloride, tetra-n-octyltin, hydrocarbon solution, infinite dilution activity coefficients.*

INTRODUCTION

Gas chromatographically measured activity coefficients of fifteen hydrocarbons at infinite dilution in tetra-n-octyltin (TOT) [1] and in tri-n-octyltin chloride (TOTC) [2] at five temperatures between 313.15 and 333.15 K were reported and discussed in two recent publications. Data for seven branched alkanes in TOT were added in a more recent paper [3].

In the present paper the results obtained in the measurement of the infinite dilution activity coefficients of twenty-eight hydrocarbons in di-n-octyltin dichloride (DOTDC) at several temperatures between 323.15 and 353.15 K, and of seven branched alkanes in TOTC at five temperatures in the interval 313.15 - 333.15 K are reported. Non-idealities observed in the binary systems formed by this group of hydrocarbons and the three alkyltin solvents are compared and their possible causes are discussed.

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EXPERIMENTAL

DOTDC was prepared by reacting equimolar quantities of TOT and tin (IV) chloride [4]. The mixture was heated at 110° C for 1 h and at 220° C for 2 h, with continuous stirring, and then fraction-distilled under reduced pressure. A light yellow product, melting between 43 and 45° C, was collected at about 170° C/ 0.2 Torr (164 - 165°C/0.16 Torr in [4]). This was further purified by using a vacuum sublimator immersed in a silicone oil bath at 80° C, with its cold finger cooled by circulating tape water; pressure was not recorded in this instance. The product obtained after discarding head and tail portions was almost white, melted at 47.0 - 48.8°C (47.5 - 48.5°C in the literature [4]), and its tin content (determined as detailed in [1]) was 28.64% by weight (28.53% calculated). Densities, measured as described in the former papers [1-3] at nine temperatures between 48.5 and 82° C, were least squares fitted to the equation

$$d(t/^\circ C) = 1.21712 - 5.8313 \times 10^{-4} t - 8.472 \times 10^{-6} t^2 + 4.13 \times 10^{-8} t^3 \tag{1}$$

Chromosorb W AW DMCS 60/80 was coated with 8.28% w/w of DOTDC in a rotary evaporator, using benzene as the volatile solvent. The dry coated support was packed into 0.22 cm i.d. x 1.0 - 2.0 m in length stainless steel tubes; the columns were conditioned for 4 h at 80° C under nitrogen flow before use. A Hewlett-Packard 5880A gas chromatograph, equipped with a flame ionization detector, was employed for the chromatographic measurements; nitrogen at flow rates of about 20 mL.min^{-1} was used as the carrier gas. The hydrocarbon solutes were of different origins, more than 99% pure, and were injected in the vapor form, either pure or in mixtures, by means of Hamilton microsyringes. Sample sizes of the order of 100 ng were simultaneously injected with a small methane sample; all the peaks were highly symmetric, and net retention times were measured to 0.001 min between the maxima of the solute and the methane peaks. Net retention time at each temperature was the mean of not less than four separate injections.

RESULTS AND DISCUSSION

Specific retention volumes were calculated from net retention times and from the values of operating parameters in the usual form [5]; from them hydrocarbons infinite dilution and zero pressure activity coefficients, $\gamma_1^\infty (0)$, were calculated as detailed in a former paper [3]. The results for twenty-eight hydrocarbons at several temperatures in DOTDC have been gathered in **Table I**, and those of seven branched alkanes in TOTC can be read in **Table II**. We estimate these results accurate to ± 0.003 from repeated mesurements performed independently. Partial molar excess enthalpies, $H_1^{E,\infty}$, estimated from the linear regression of ln $\gamma_1^\infty (0)$ against 1/T, have been also included in the tables.

The solutes can be split into two groups, according with their behavior in the three solvents. The first group includes all the solutes, excepting the aromatic hydrocarbons; their activity coefficients increase noticeably in passing from TOT to TOTC, and suffer a further increase in passing from TOTC to DOTDC. Typical values for solutes of this group at 50° C are 0.58 - 0.70 in TOT, 0.80 - 1.00 in TOTC, and 1.40 - 1.70 in DOTDC; when the activity coefficients in DOTDC at 50° C are plotted against the corresponding values in TOT, the points corresponding to solutes of this group fall on a commom line, with 0.985 as correlation

coefficient, and the same relationship is shown by the data in the solvents TOTC and TOT, the correlation coefficient being 0.982 in this case. The aromatic solutes constitute the second group of solutes; their activity coefficients suffer only minor increases in passing from TOT to one of the chlorinated solvents, and are smaller than unity in the three stationary phases.

TABLE I
Infinite Dilution Activity Coefficients and Partial Molar Excess Enthalpies of Hydrocarbons in DOTDC

SOLUTE	50	55	60	65	70	75	80	$H_1^{E,\infty} \pm s$ [a],[b]
n-Hexane	1.414	1.386	1.357		1.332			2740 ± 380
2-Methylpentane	1.451		1.415	1.401	1.396		1.375	1680 ± 160
3-Methylpentane	1.369		1.338	1.324	1.322		1.297	1660 ± 150
2,2-Dimethylbutane	1.400		1.353	1.340	1.323		1.306	2190 ± 240
n-Heptane	1.506		1.454	1.441	1.422	1.404		2590 ± 130
2-Methylhexane	1.554		1.508		1.479		1.454	2080 ± 110
3-Methylhexane	1.491		1.449		1.423		1.398	2000 ± 140
2,3-Dimethylpentane	1.382		1.334	1.315	1.300		1.279	2450 ± 230
2,4-Dimethylpentane	1.577	1.542	1.511		1.484			2770 ± 410
n-Octane	1.618		1.559	1.539	1.519	1.497	1.483	2750 ± 110
2-Methylheptane	1.663		1.613		1.579		1.551	2200 ± 150
4-Methylheptane	1.615	1.578	1.544		1.510			3080 ± 390
2,2-Dimethylhexane	1.666		1.604		1.568		1.536	2540 ± 230
2,5-Dimethylhexane	1.681	1.641	1.606		1.568			3170 ± 360
2,2,4-Trimethylpentane	1.616		1.570		1.523		1.495	2520 ± 140
2,3,4-Trimethylpentane			1.434	1.419	1.398	1.382	1.367	2400 ± 70
Cyclohexane	1.013		0.988		0.959		0.956	1950 ± 360
Methylcyclohexane	1.095		1.057	1.041	1.032		1.015	2400 ± 240
Ethylcyclohexane	1.226		1.191		1.168		1.149	2020 ± 160
1-Hexene	1.179		1.146	1.135	1.127		1.119	1650 ± 270
1-Heptene	1.273		1.234	1.218	1.209		1.193	2050 ± 250
1-Octene	1.372		1.344		1.310		1.293	1910 ± 140
Benzene	0.682		0.671		0.668		0.667	680 ± 220
Toluene			0.725	0.725	0.724	0.722	0.720	390 ± 70
Ethylbenzene	0.800		0.805		0.801		0.801	-50 ± 220
o-Xylene			0.775	0.773	0.772	0.770	0.769	380 ± 40
m-Xylene			0.797	0.796	0.795	0.793	0.794	230 ± 70
p-Xylene			0.788	0.788	0.788	0.786	0.785	210 ± 50

[a] Units: $J.mol^{-1}$. [b] s: standard deviation.

In order to attempt an interpretation for this behavior the combinatorial and the free volume contributions to the infinite dilution activity coefficients, γ_1^∞ (comb) and γ_1^∞ (fv) respectively, were computed by means of the corresponding expressions [1] deduced from the model of Flory [6], using the reduction parameters listed in the former publications for the solutes, for TOT and for TOTC [1-3]; for DOTDC a molar volume reduction parameter $V_2^* = 282.8$ $cm^3.mol^{-1}$ was computed from eq.(1). The activity coefficients were considered as resulting from the following contributions:

$$\ln \gamma_1^\infty (0) = \ln \gamma_1^\infty (comb) + \ln \gamma_1^\infty (fv) + \ln \gamma_1^\infty (res) \qquad (2)$$
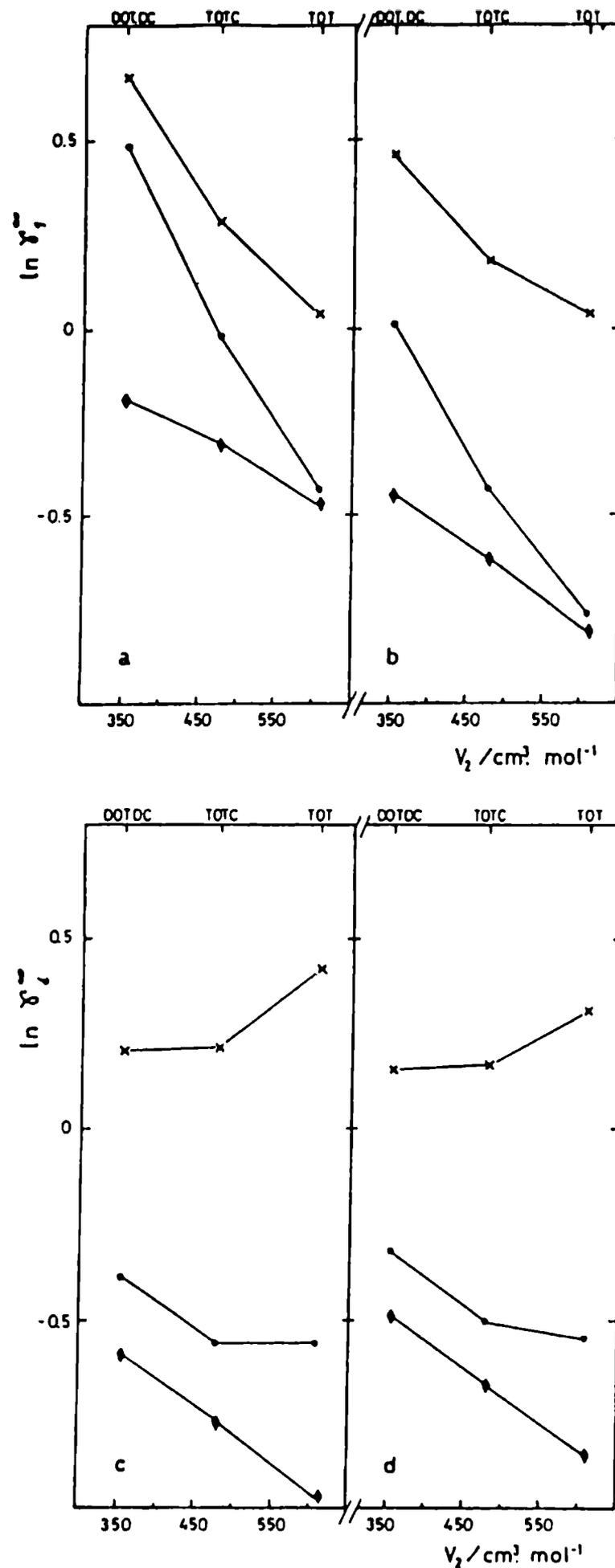
Fig. 1.- Plot of the infinite dilution activity coefficients against the solvent molar volume at 50° C, for four representative solutes. (a) n-Octane; (b) cyclohexane; (c) benzene; (d) toluene. (•) Experimental activity coefficients; (◆) combinatorial plus free volume contributions; (x) residual contributions.

where γ_1^∞ (res) is a residual value, obtained by substracting both theoretical contributions from the experimental value, to which a physical interpretation has to be assigned. In **Figure 1** the values of ln γ_1^∞ (0), of the sum ln γ_1^∞ (comb) + ln γ_1^∞ (fv), and of ln γ_1^∞ (res) have been plotted against the solvent molar volume for two solutes belonging to the first group and for two aromatic solutes, at 50° C.

TABLE II

Infinite Dilution Activity Coefficients and Partial Molar Excess Enthalpies of Hydrocarbons in TOTC

			t/° C			
SOLUTE	40	45	50	55	60	$H_1^{E,\infty} \pm s^{a,b}$
2-Methylpentane	0.903	0.895	0.884	0.880	0.878	1280 ± 180
3-Methylpentane	0.860	0.852	0.844	0.839	0.834	1360 ± 100
2-Methylhexane	0.956	0.946	0.935	0.928	0.922	1590 ± 90
2,4-Dimethylpentane	0.979	0.969	0.959	0.952	0.946	1490 ± 100
4-Methylheptane	0.987	0.976	0.966	0.958	0.952	1580 ± 90
2,2-Dimethylhexane	1.028	1.015	1.002	0.993	0.985	1850 ± 100
2,5-Dimethylhexane	1.030	1.019	1.007	0.998	0.991	1690 ± 80

[a] Units: J.mol^{-1}. [b] s: standard deviation.

In discussing the results plotted in **Fig. 1** it has to be pointed out firstly that since reduced volumes of the three solvents differ very little, the free volume contributions for a given solute are almost equal in the three stationary phases. Therefore the drops observed for the plots of ln γ_1^∞ (comb) + ln γ_1^∞ (fv) against the solvent molar volume have to be attributed to decreasing values of the combinatorial contribution resulting from important increases in solvent molar volume in the direction DOTDC < TOTC <TOT. The residual contribution is very small for solutes of the first group in TOT, but increases markedly when one chlorine atom replaces an octyl group in the solvent molecule, and even more by the introduction of a second chlorine atom; in our opinion this effect is purely interactional, and reflects very large differences between the force fields in the vecinity of the hydrocarbonaceous solute chain and of the solvent halogen atoms. Benzene, on the other side, shows an important residual contribution in TOT that decreases by the introduction of halogen atoms in the solvent molecule; this trend can be explained in terms of interactional effects resulting from dipole induction into the aromatic nucleus by the highly polar chlorinated solvents.

Partial molar excess enthalpies for the same group of four solutes have been plotted against the solvent molar volume in **Fig. 2**. All the systems display endothermal mixing at infinite dilution; however the chlorination of the solvent molecules produces opposite effects in solutes of the two groups. These trends are coherent with those described in the previous paragraph.
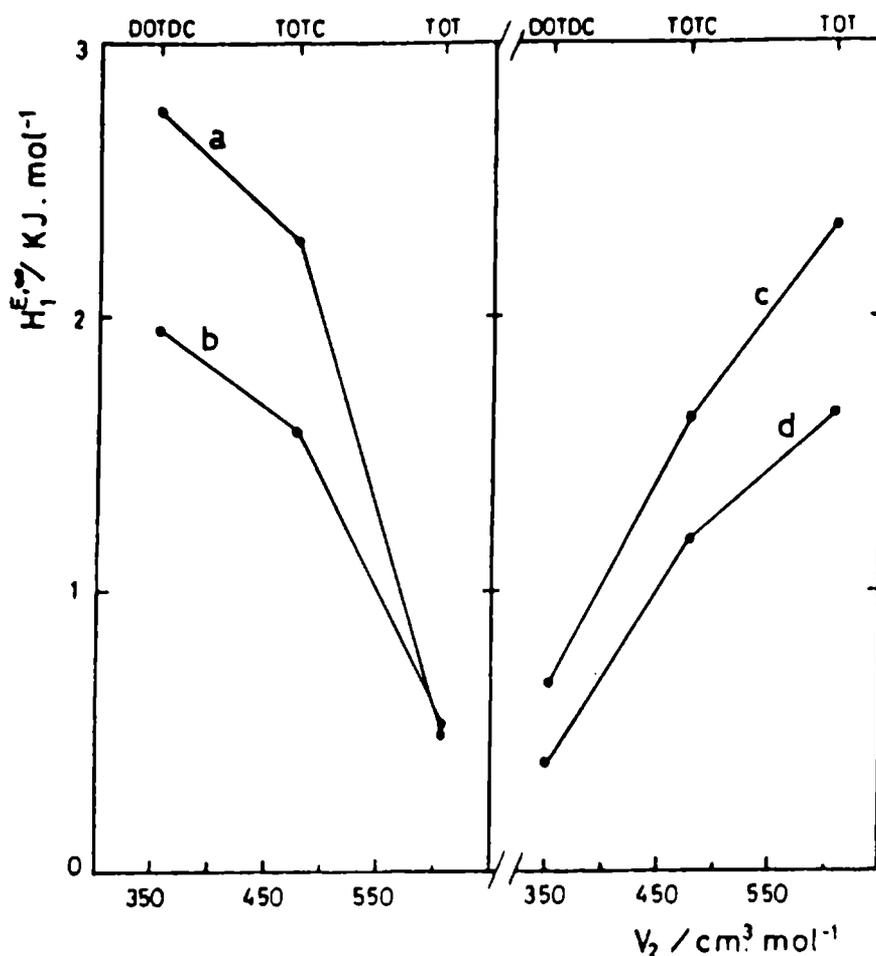
Fig. 2.- Infinite dilution partial molar excess enthalpy of four solutes against the solvent molar volume. Solute identification as in Fig. 1.

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