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CORRELATION OF HYDROCARBON ACTIVITY COEFFICIENTS WITH SOLUBILITY PARAMETERS FOR PHTHALATE ESTERS

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SUMMARY

Eight phthalate esters (diethyl, di-*n*-butyl, diisobutyl, dicyclohexyl, di-2-ethyl-hexyl, diisodecyl, butyl benzyl and butyl ethylhexyl phthalate), commonly used as stationary phases in gas chromatography and as plasticizers for polymeric materials, have been characterized by determining the polar and non-polar contributions to the solubility parameter in accordance with the theory of Weimer and Prausnitz.

The results obtained are in good agreement with the activity coefficients at infinite dilution determined previously by gas chromatography.

The influence of the nature of the esterifying alcohols is discussed. Good agreement was found between the order of the "polarity indices" determined in the present work and the few data reported in the literature by Hansen.

INTRODUCTION

The solubility parameter theory provides an interpretation of the interaction phenomena that occur in the liquid state; so equilibrium data can be obtained. The polar and non-polar components of the energies involved in these interactions can be determined, according to Weimer and Prausnitz[1], by evaluating the energy contributions λ and τ.

This theory has been applied on several occasions[2–4]. In general, the error of prediction does not exceed 10–20 %, and this accuracy is considered to be satisfactory; higher errors (100% or more) are encountered with alcohols and other compounds with associated molecules.

According to Weimer and Prausnitz[1], the parameters λ and τ are related to the activity coefficients at infinite dilution by the equation

$$\ln \gamma_2^{\infty} = \frac{v_2}{RT} \left[(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 - 2\,\psi_{12} \right] + \left[\ln \frac{v_2}{v_1} + \left(1 - \frac{v_2}{v_1} \right) \right] \quad (1)$$

where subscript 1 indicates the solvent and subscript 2 the solute.

In this paper, we report the results obtained by applying the solubility parameter theory to a series of phthalate esters for which few data are available in the

TABLE I

MOLAR VOLUMES (v_2) AND POLAR (τ_2) AND NON-POLAR (λ_2) CONTRIBUTIONS TO THE SOLUBILITY PARAMETER AT 25° FOR THE HYDROCARBON SOLUTES

Solute	v_2 (ml/mole)	λ_2	τ_2
n-Pentane	116.1	7.08	0
n-Hexane	130.0	7.35	0
n-Heptane	148.0	7.47	0
n-Octane	164.0	7.59	0
1-Pentene	110.0	7.20	1.56
1-Hexene	125.9	7.30	1.52
1-Heptene	141.5	7.40	1.30
1-Octene	155.6	7.53	1.25
Cyclohexane	108.7	8.12	0
Methylcyclohexane	128.2	7.86	0
Ethylcyclohexane	143.5	7.85	0
Benzene	89.3	8.52	3.46
Toluene	108.0	8.32	3.16
Ethylbenzene	124.2	8.21	3.15

literature (diethyl phthalate, DEP; di-n-butyl phthalate, DBP; diisobutyl phthalate, DIBP; dicyclohexyl phthalate, DCyC$_6$P; di-2-ethylhexyl phthalate, D2EEP; diisodecyl phthalate, DIDP; butyl benzyl phthalate, BBP; and butyl ethylhexyl phthalate, BEEP). Paraffins, olefins, cycloparaffins and aromatic hydrocarbons were used as solutes.

RESULTS AND DISCUSSION

The values of the molar volumes (v_2) and those of the polar (τ_2) and non-polar (λ_2) contributions to the solubility parameters at 25 ° for the hydrocarbon solutes are reported in Table I. These values were obtained on the basis of the concept of homomorph, as suggested by Weimer and Prausnitz[1] and by Bondi and Simkin[5]. In the selection of the homomorphs, structures were taken into greater account than molar volumes. Accordingly, we have previously drawn two homomorphism diagrams for linear and cyclic molecules, respectively, considering only the paraffinic and the cycloparaffinic molecule as non-polar[4].

Hence, if the molar volume of a substance is known, by means of the homomorphism diagrams it is possible to determine the non-polar contribution of the vaporization energy ($\Delta U_{i,np}$) and, by means of the relationships $\lambda_i = \sqrt{\dfrac{\Delta U_{i,np}}{v_i}}$, the λ_i value.

The polar contribution τ_i is evaluated by the equation

$$\tau_i^2 = \frac{\Delta U_i}{v_i} - \lambda_i^2 \tag{2}$$

where ΔU_i is the total vaporization energy.

TABLE II

MOLAR VOLUMES (v_1), POLAR (τ_1) AND NON-POLAR (λ_1) CONTRIBUTIONS TO THE SOLUBILITY PARAMETER, POLARITY INDICES (I_p) AND $I_{p,ll}$ VALUES FOR THE PHTHALATES AT 25°

Solvent	v_1 (ml/mole)	λ_1	τ_1	I_p	$I_{p,ll}$
DEP	200.0	8.68	5.80	0.556	
DBP	273.7	7.96	4.11	0.459	0.51
DIBP	268.0	8.45	4.95*	0.505	
DCyC$_6$P	287.0	8.54	4.64	0.477	
D2EEP	396.0	8.22	4.10	0.446	0.40
DIDP	461.0	7.88	4.18	0.469	
BBP	282.0	9.05	5.10	0.491	0.58
BEEP	335.9	7.60	3.42	0.410	
DMP*					0.59

* DMP = Dimethylphthalate.

The ψ_{12} term in eqn. 1 depends on $(\tau_1 - \tau_2)^2$ (refs. 1 and 6):

$$\psi_{12} = m(\tau_1 - \tau_2)^2 \tag{3}$$

Then, substituting eqn. 3 into eqn. 1, we obtain

$$\ln \gamma_2^\infty = \frac{v_2}{RT}\left[(\lambda_1 - \lambda_2)^2 + (1 - 2m)(\tau_1 - \tau_2)^2\right] + \left[\ln \frac{v_2}{v_1} + \left(1 - \frac{v_2}{v_1}\right)\right] \tag{4}$$

where the value of $(1 - 2m)$ is characteristic for each class of solutes: 0.202 for paraffins and cycloparaffins, 0.245 for olefins and 0.285 for aromatics[4].
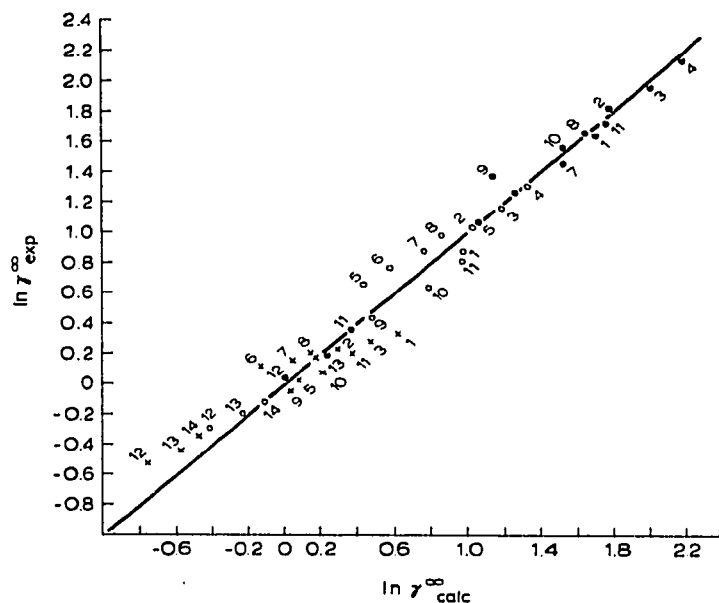

Fig. 1. Comparison between experimental and calculated (according to eqn. 4) activity coefficients at 25° in DEP(●), DIDP(×) and DCyC$_6$P(○).
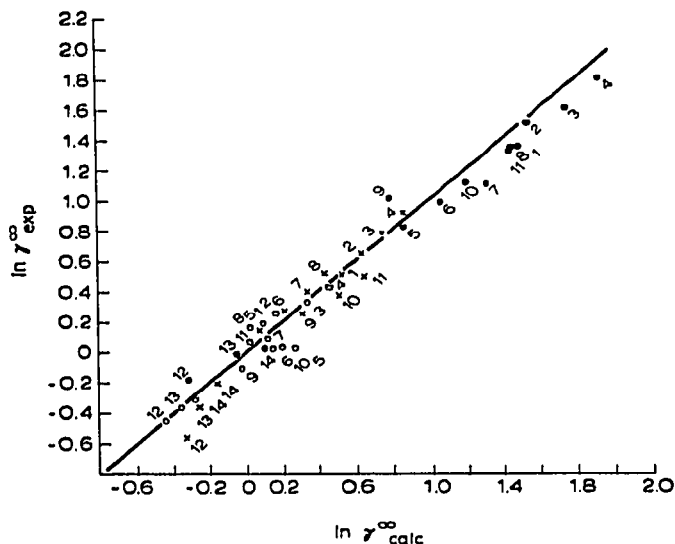
Fig. 2. Comparison between experimental and calculated (according to eqn. 4) activity coefficients at 25° in DBP ($\times$), BBP ($\bullet$) and BEEP ($\bigcirc$).

On the basis of the λ_2 and τ_2 values obtained for the solutes and of the activity coefficients of the same solutes in phthalates given in a previous paper[7], we calculated the polar and non-polar contributions to the solubility parameters for the solvents studied (Table II). The reliability of these values can be appraised by taking into consideration the agreement between the values of the activity coefficients calculated on the basis of eqn. 4, $\ln \gamma^{\infty}_{\text{calc.}}$, and those obtained experimentally, $\ln \gamma^{\infty}_{\text{exp}}$. (Figs. 1–3).
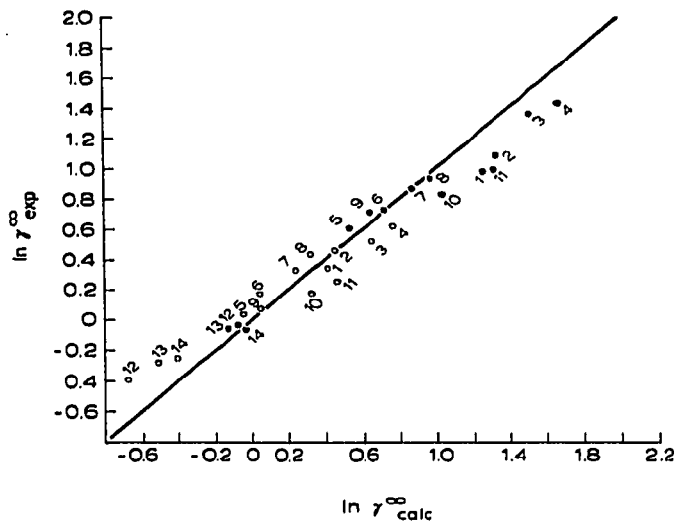

Fig. 3. Comparison between experimental and calculated (according to eqn. 4) activity coefficients at 25° in D2EEP ($\bigcirc$) and DIBP ($\bullet$).

The agreement is considered to be satisfactory; the deviations are less than 20% (average 7%).

For a more detailed characterization of the solvents, the "polarity index", $I_p = \tau/\sqrt{\lambda^2 + \tau^2}$, can be used. A comparison of the polarity indices (Table II) shows that the phthalate with the highest polarity index is DEP, while lower indices are found for the esters of long-chain alcohols.

A high polarity contribution is encountered in BBP. This effect can be ascribed to the presence of the benzyl group; the fact that BBP has a polarity index lower than that of DEP is probably due to a better balance between the benzyl and the phthalate groups in terms of symmetry.

It is interesting to compare DIBP with DBP. The higher polarity of the former may be due to the fact that its main chain is shorter, and so its polarity index is closer to that of DEP.

The peculiar behaviour of BEEP with respect to DBP and D2EEP should be noted. In fact, the polarity index of BEEP is not intermediate between those of the other two, but is lower. A similar situation had been reported previously for activity coefficients[7], where the hypothesis of intramolecular interactions was put forward.

The polarity sequence in Table II was compared with polarities derived from the few data reported by Hansen[8], who split the solubility parameter into three contributions: δ_p, δ_{II} and δ_d, and defined a δ_a parameter for the non-dispersional contribution as $\delta_a = \sqrt{\delta_p^2 + \delta_{II}^2}$.

A comparison was made by evaluating a new polarity index,

$$I_{p,II} = \frac{\delta_a}{\sqrt{\delta_d^2 + \delta_p^2 + \delta_{II}^2}}$$

from the data of Hansen, in analogy with our polarity index (Table II). The agreement in the sequence of these two types of polarity indices appears to be good.

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