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ACTIVITY COEFFICIENTS OF HYDROCARBONS IN PHTHALATES

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SUMMARY

Activity coefficients at infinite dilution of hydrocarbons in eight phthalates at 25, 50, 75, 100 and 125 °C were determined by gas chromatography. The effects of the nature of the esterifying alcohols and of the solute and that of temperature are discussed. A non-linear behaviour of $\ln \gamma_i^\infty$ *versus* $1/T$ was found; hence the excess partial molar heat capacities at infinite dilution of the solutes in the phthalates studied ($\bar{C}_p^{E,\infty}$) were evaluated over the temperature range 25–125 °C and a relationship between $\ln \gamma_i^\infty$ and T (°K) was obtained.

INTRODUCTION

Gas chromatography can be employed with good results to obtain equilibrium data in solutions at infinite dilution. These data, which indicate the solute–solvent interactions, permit a rigorous characterization of the solvents to be made, thereby opening up interesting prospects for the employment of these materials for analytical and industrial purposes.

This paper reports the results obtained for a series of phthalate esters normally used as stationary phases in gas–liquid chromatography (GLC)[1,2] and as plasticizers for binders and plastics[3].

Thermodynamic data obtained at many temperatures have shown the non-linear variation of the logarithm of the activity coefficients of the solutes at infinite dilution as a function of $1/T$. Accordingly, we determined by means of the following relationships[4]

$$R \left(\frac{\partial \ln \gamma_i^\infty}{\partial 1/T} \right)_P = \Delta \bar{H}_i^{E,\infty} \tag{1}$$

$$\left(\frac{\partial \bar{H}_i^{E,\infty}}{\partial T} \right)_P = \bar{C}_{p\,i}^{E,\infty} \tag{2}$$

the excess partial molar heat capacities at infinite dilution ($\bar{C}_p^{E,\infty}$) of various hydrocarbon solutes in the stationary phases studied.

EXPERIMENTAL

Solute–solvent interactions were evaluated by means of the activity coefficient, which depends on the gas chromatographic retention parameters as follows[5,6]:

$$\ln \gamma_i^\infty = \ln \left(\frac{273\,R}{v_g^0\,p_i^0\,M_s} \right) - \frac{(B_{ii} - v_i^0)\,p_i^0}{RT} + \frac{(2\,B_{ij} - V_i)\,P}{RT} \tag{3}$$

The parameters in eqn. 3 were calculated in accordance with Desty and Swanton[6]; the retention time was determined according to a criterion proposed in a previous paper[7].

The GLC apparatus was a thermal conductivity chromatograph (Fractovap Model B, Carlo Erba, Milan, Italy).

Paraffins, olefins, cycloparaffins and aromatic hydrocarbons (Fluka, Buchs, Switzerland; BDH, Poole, Great Britain) were used as solutes and the following phthalates, suitably dried, were used as stationary phases: 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) (Monsanto, St. Louis, Mo., U.S.A.; Union Carbide, New York, N.Y., U.S.A.; Bayer, Leverkusen, G.F.R.).

RESULTS AND DISCUSSION

Tables I–VIII report the natural logarithms of the activity coefficients of the various hydrocarbons at infinite dilution at 25, 50, 75, 100 and 125 °C in the different stationary phases. The values of the activity coefficients at 25 °C for BBP, DCyC$_6$P, DIDP, D2EEP, DIBP and BEEP as well as the values at 125 °C for DBP, DIBP and at 100 and 125 °C for DEP were obtained by extrapolation of the specific retention volumes.

TABLE I

NATURAL LOGARITHM OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR HYDROCARBONS IN DIETHYL PHTHALATE

Compound	25 °C	50 °C	75 °C	100 °C	125 °C
n-Pentane	1.64	1.37	1.16	1.01	0.89
n-Hexane	1.82	1.50	1.29	1.11	0.98
n-Heptane	1.97	1.65	1.40	1.21	1.08
n-Octane	2.14	1.79	1.53	1.34	1.21
1-Pentene	1.07	0.93	0.84	0.79	0.74
1-Hexene	1.25	1.09	0.98	0.89	0.84
1-Heptene	1.45	1.23	1.08	0.97	0.90
1-Octene	1.67	1.38	1.18	1.04	0.95
Cyclohexane	1.39	1.12	0.95	0.76	0.65
Methylcyclohexane	1.56	1.27	1.07	0.86·	0.76
Ethylcyclohexane	1.74	1.42	1.22	1.03	0.93
Benzene	0.04	−0.05	−0.11	−0.16	−0.17
Toluene	0.20	0.09	0.02	−0.03	−0.05
Ethylbenzene	0.36	0.22	0.15	0.11	0.10

TABLE II

NATURAL LOGARITHM OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR HYDROCARBONS IN DI-*n*-BUTYL PHTHALATE

Compound	25 °C	50 °C	75 °C	100 °C	125 °C
n-Pentane	0.54	0.47	0.42	0.39	0.37
n-Hexane	0.66	0.56	0.52	0.49	0.47
n-Heptane	0.78	0.68	0.63	0.59	0.58
n-Octane	0.91	0.79	0.73	0.68	0.65
1-Pentene	0.15	0.13	0.11	0.10	0.092
1-Hexene	0.27	0.23	0.21	0.20	0.19
1-Heptene	0.40	0.35	0.33	0.32	0.31
1-Octene	0.52	0.47	0.44	0.42	0.41
Cyclohexane	0.27	0.22	0.20	0.18	0.17
Methylcyclohexane	0.38	0.31	0.29	0.27	0.26
Ethylcyclohexane	0.50	0.42	0.39	0.38	0.37
Benzene	−0.55	−0.61	−0.65	−0.66	−0.67
Toluene	−0.35	−0.46	−0.50	−0.54	−0.56
Ethylbenzene	−0.19	−0.31	−0.39	−0.43	−0.45

Good agreement was found between the experimental data obtained for paraffins and cycloparaffins in DEP and the data calculated by extrapolation of the values given by Petsev and Dimitrov[8] for the same solutes in the phthalates of homologous *n*-alkanols. We found agreement with the data for aromatic hydrocarbons in DIBP[9], whereas for paraffins and cycloparaffins substantial discrepancies were found between our experimental values and those given by Petsev and Dimitrov[8]. These discrepancies may be accounted for by the different working conditions; whereas our results were obtained by using a stationary phase:support ratio of 0.25 (as suggested by Desty and Swanton[6]), Petsev and Dimitrov used a ratio of 0.15; this low figure may cause, according to Martire[10], adsorption of the solute because the surface of the support is not fully covered with the stationary phase.

TABLE III

NATURAL LOGARITHM OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR HYDROCARBONS IN DIISOBUTYL PHTHALATE

Compound	25 °C	50 °C	75 °C	100 °C	125 °C
n-Pentane	0.97	0.77	0.61	0.53	0.50
n-Hexane	1.11	0.90	0.72	0.62	0.58
n-Heptane	1.28	1.02	0.82	0.73	0.65
n-Octane	1.45	1.15	0.93	0.81	0.72
1-Pentene	0.62	0.48	0.38	0.32	0.29
1-Hexene	0.74	0.58	0.49	0.41	0.39
1-Heptene	0.86	0.68	0.58	0.50	0.46
1-Octene	0.95	0.80	0.66	0.59	0.55
Cyclohexane	0.71	0.57	0.45	0.37	0.31
Methylcyclohexane	0.85	0.67	0.53	0.45	0.38
Ethylcyclohexane	1.00	0.78	0.62	0.52	0.44
Benzene	−0.15	−0.24	−0.29	−0.30	−0.31
Toluene	−0.035	−0.13	−0.18	−0.19	−0.20
Ethylbenzene	0.061	−0.039	−0.087	−0.095	−0.11

TABLE IV

NATURAL LOGARITHM OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR HYDROCARBONS IN DICYCLOHEXYL PHTHALATE

Compound	25 °C	50 °C	75 °C	100 °C	125 °C
n-Pentane	0.87	0.81	0.77	0.74	0.71
n-Hexane	1.01	0.91	0.84	0.80	0.75
n-Heptane	1.16	1.02	0.92	0.87	0.82
n-Octane	1.31	1.13	1.00	0.94	0.88
1-Pentene	0.67	0.56	0.51	0.46	0.44
1-Hexene	0.77	0.65	0.59	0.55	0.51
1-Heptene	0.88	0.74	0.68	0.63	0.60
1-Octene	0.98	0.83	0.76	0.72	0.68
Cyclohexane	0.43	0.36	0.32	0.30	0.28
Methylcyclohexane	0.64	0.52	0.48	0.45	0.43
Ethylcyclohexane	0.83	0.71	0.62	0.60	0.58
Benzene	−0.29	−0.33	−0.34	−0.35	−0.36
Toluene	−0.20	−0.25	−0.27	−0.28	−0.29
Ethylbenzene	−0.11	−0.17	−0.19	−0.20	−0.21

A comparison of the results obtained in this work with the few data on activity coefficients available in the literature (only at 120 °C)[8,9] revealed a series of regularities related to variations in structural parameters, which can be summarized as follows:

(1) Effect of the nature of the esterifying alcohol

The higher the number of carbon atoms in the esterifying alcohol, the lower are the activity coefficients, and *vice versa* (DEP–DIDP).

(a) Straight-chain alcohols. By comparing the results obtained for DEP and DBP with those available in the literature[8] for di-n-hexyl phthalate, di-n-octyl phthalate and di-n-decyl phthalate, it can be seen that the activity coefficients decrease linearly with increasing molecular weight of the alcohol.

(b) Branched-chain alcohols. By comparing the results obtained for DIDP,

TABLE V

NATURAL LOGARITHM OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR HYDROCARBONS IN DI-2-ETHYLHEXYL PHTHALATE

Compound	25 °C	50 °C	75 °C	100 °C	125 °C
n-Pentane	0.35	0.26	0.21	0.20	0.20
n-Hexane	0.45	0.33	0.29	0.27	0.26
n-Heptane	0.54	0.41	0.36	0.33	0.32
n-Octane	0.63	0.48	0.42	0.39	0.38
1-Pentene	0.041	0.012	0.001	−0.010	−0.015
1-Hexene	0.19	0.13	0.11	0.10	0.085
1-Heptene	0.34	0.25	0.22	0.21	0.17
1-Octene	0.45	0.37	0.33	0.30	0.28
Cyclohexane	0.094	0.028	−0.007	−0.025	−0.040
Methylcyclohexane	0.19	0.098	0.042	0.011	−0.010
Ethylcyclohexane	0.28	0.16	0.085	0.051	0.031
Benzene	−0.39	−0.43	−0.45	−0.46	−0.46
Toluene	−0.29	−0.37	−0.40	−0.41	−0.42
Ethylbenzene	−0.25	−0.34	−0.37	−0.38	−0.39

TABLE VI

NATURAL LOGARITHM OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR HYDROCARBONS IN DIISODECYL PHTHALATE

Compound	25 °C	50 °C	75 °C	100 °C	125 °C
n-Pentane	0.18	0.055	−0.032	−0.072	−0.10
n-Hexane	0.23	0.11	0.0012	−0.031	−0.076
n-Heptane	0.29	0.14	0.050	−0.0062	−0.027
n-Octane	0.33	0.20	0.11	+0.045	0.0045
1-Pentene	0.070	−0.078	−0.13	−0.16	−0.17
1-Hexene	0.12	−0.034	−0.092	−0.13	−0.16
1-Heptene	0.16	0.0096	−0.060	−0.11	−0.13
1-Octene	0.20	0.040	−0.033	−0.069	−0.093
Cyclohexane	−0.053	−0.15	−0.23	−0.27	−0.29
Methylcyclohexane	0.081	−0.051	−0.15	−0.20	−0.24
Ethylcyclohexane	0.20	0.075	−0.077	−0.14	−0.17
Benzene	−0.54	−0.62	−0.67	−0.68	−0.69
Toluene	−0.44	−0.53	−0.58	−0.59	−0.60
Ethylbenzene	−0.34	−0.45	−0.50	−0.51	−0.52

D2EEP and DIBP with those available in the literature[8,9] for di-n-decyl phthalate, di-n-octyl phthalate and DBP, it can be seen that the activity coefficients are higher for the esters of branched-chain alcohols, and that they decrease with increasing molecular weight of the esterifying alcohol.

(c) *Cyclic alcohols.* A comparison of the data available for DCyC$_6$P, diphenyl phthalate and di-n-hexyl phthalate[8] shows that the activity coefficients increase in the order di-n-hexyl phthalate < DCyC$_6$P < diphenyl phthalate. The effect of the cyclic structure is further confirmed by comparing the results obtained in BBP and DBP; the activity coefficient is higher in BBP than in DBP, in spite of the greater number of carbon atoms present in the benzyl alcohol.

(d) *BBP–BEEP.* The substitution of a benzyl for a 2-ethylhexyl group in-

TABLE VII

NATURAL LOGARITHM OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR HYDROCARBONS IN BUTYL BENZYL PHTHALATE

Compound	25 °C	50 °C	75 °C	100 °C	125 °C
n-Pentane	1.35	1.17	1.03	0.94	0.87
n-Hexane	1.51	1.29	1.15	1.04	0.97
n-Heptane	1.62	1.43	1.26	1.15	1.07
n-Octane	1.81	1.56	1.37	1.27	1.23
1-Pentene	0.83	0.71	0.65	0.61	0.59
1-Hexene	1.01	0.86	0.79	0.74	0.69
1-Heptene	1.11	1.10	0.92	0.87	0.81
1-Octene	1.34	1.16	1.05	0.99	0.95
Cyclohexane	1.01	0.83	0.73	0.61	0.58
Methylcyclohexane	1.12	0.96	0.84	0.78	0.69
Ethylcyclohexane	1.32	1.12	0.98	0.91	0.84
Benzene	−0.18	−0.24	−0.26	−0.27	−0.28
Toluene	−0.011	−0.076	−0.10	−0.11	−0.12
Ethylbenzene	0.053	−0.021	−0.049	−0.059	−0.065

TABLE VIII

NATURAL LOGARITHM OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR HYDROCARBONS IN BUTYL ETHYLHEXYL PHTHALATE

Compound	25 °C	50 °C	75 °C	100 °C	125 °C
n-Pentane	0.19	0.12	0.082	0.063	0.048
n-Hexane	0.28	0.19	0.15	0.12	0.11
n-Heptane	0.35	0.26	0.22	0.19	0.18
n-Octane	0.43	0.33	0.28	0.26	0.25
1-Pentene	−0.056	−0.10	−0.11	−0.11	−0.12
1-Hexene	0.032	−0.031	−0.037	−0.045	−0.058
1-Heptene	0.107	0.045	0.035	0.025	0.015
1-Octene	0.18	0.12	0.11	0.095	0.087
Cyclohexane	−0.11	−0.17	−0.19	−0.21	−0.22
Methylcyclohexane	−0.021	−0.075	−0.10	−0.12	−0.13
Ethylcyclohexane	0.078	0.015	−0.015	−0.037	−0.048
Benzene	−0.45	−0.51	−0.53	−0.38	−0.40
Toluene	−0.36	−0.42	−0.45	−0.46	−0.47
Ethylbenzene	−0.30	−0.35	−0.37	−0.54	−0.55

creases the activity coefficients much more that would be expected from the difference of one carbon atom (ln $\gamma^{\infty}_{n\text{-hexane}}$ in BBP = 1.5, in BEEP = 0.28). A similar effect is found for the pair BBP and DBP: the activity coefficients are higher in BBP than in DBP, although DBP is based on a short-chain esterifying alcohol instead of the benzyl alcohol.

(e) The peculiar behaviour of BEEP should be noted; among DBP, D2EEP and DEEP the lowest values of activity coefficients at infinite dilution are found in BEEP, whereas intermediate values would be expected; intramolecular interactions probably account for this effect.

(2) Effect of the nature of the solutes

(a) The activity coefficients increase linearly with the number of carbon atoms within each class of hydrocarbons considered.

(b) If the number of carbon atoms in hydrocarbon solutes of different classes remains constant, the activity coefficients decrease starting from paraffins, through olefins, cycloparaffins and aromatic hydrocarbons; the last generally have activity coefficients lower than unity. The highest activity coefficients were found in BBP and DEP for all of the hydrocarbons examined.

(3) Effect of temperature

The natural logarithm of the activity coefficients at infinite dilution increase with decreasing temperature and, within each homologous series, they converge towards a common value at very high temperatures. By plotting these values versus $1/T$, a non-linear behaviour can be seen, as shown in Fig. 1, in which the variation of ln γ_i^{∞} is reported for four solutes in DEP as stationary phase. From eqns. 1 and 2 and applying the least-squares method, we evaluated the dependence of ln γ_i^{∞} on T, which is given by the equation

$$\ln \gamma_i^{\infty} = \left(-\frac{\bar{C}_p^{E,\infty}}{R}\right) \ln T + \frac{A}{R} \cdot \frac{1}{T} + B \qquad (4)$$
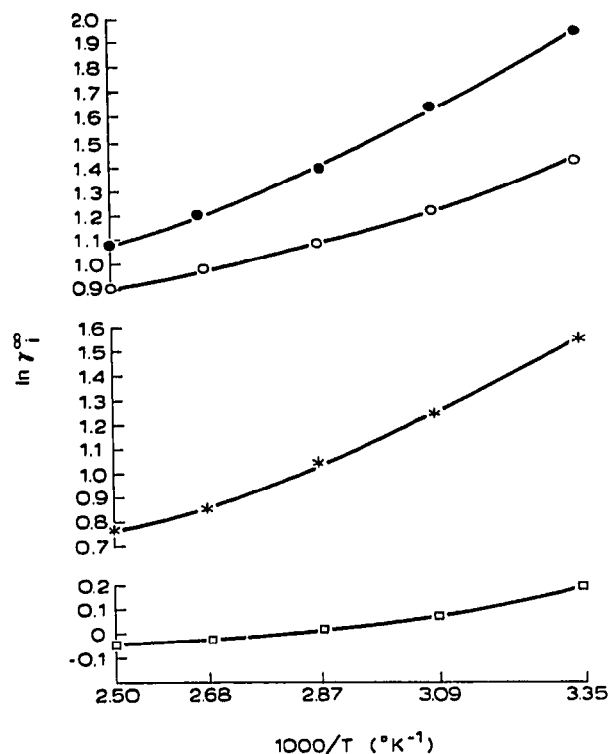
Fig. 1. Natural logarithms of activity coefficients at infinite dilution of *n*-heptane (●), 1-heptene (○), methylcyclohexane (✳) and toluene (□) in diethyl phthalate.

TABLE IX

VALUES OF PARAMETERS IN EQN. 4 FOR DEP, DBP, DIBP AND DCyC$_6$P STATIONARY PHASES

Stationary phase	Solute	$\dfrac{\bar{C}_p^{E,\infty}}{R}$	$\dfrac{A}{R}$	B
DEP	*n*-Heptane	5.93	3090.67	−42.18
	1-Heptene	5.36	2493.11	−37.45
	Methylcyclohexane	3.14	2026.42	−23.13
	Toluene	3.58	1525.67	−25.31
DBP	*n*-Heptane	3.46	1424.67	−23.71
	1-Heptene	1.80	724.32	−12.28
	Methylcyclohexane	2.08	854.70	−14.34
	Toluene	2.90	1245.86	−21.05
DIBP	*n*-Heptane	9.68	4070.74	−67.52
	1-Heptene	4.98	2182.68	−34.84
	Methylcyclohexane	4.97	2264.80	−35.06
	Toluene	4.92	1883.20	−34.39
DCyC$_6$P	*n*-Heptane	4.42	1921.91	−30.47
	1-Heptene	3.87	1661.15	−26.74
	Methylcyclohexane	3.88	1579.03	−26.77
	Toluene	1.80	724.32	−12.88

In Tables IX and X are reported, as examples, the values of $\bar{C}_p^{E,\infty}$, A and B in the temperature range 25–125 °C for four solutes. Fig. 1 clearly shows that within this temperature range the $\bar{C}_p^{E,\infty}$ values are higher in the upper part of the plot, i.e., at lower temperatures. From these data it can seen that the highest $\bar{C}_p^{E,\infty}$ values are found for for the phthalates based on branched-chain alcohols, whereas lower $\bar{C}_p^{E,\infty}$ values are found for the phthalates based on the corresponding straight-chain alcohols; DBP shows the lowest $\bar{C}_p^{E,\infty}$ values. Moreover, it is apparent that the substitution of a butyl for a benzyl group increases the values of $\bar{C}_p^{E,\infty}$. For the solutes, the highest values of $\bar{C}_p^{E,\infty}$ are found for the paraffins.

TABLE X

VALUES OF PARAMETERS IN EQN. 4 FOR D2EEP, DIDP, BBP AND BEEP STATIONARY PHASES

Stationary phase	Solute	$-\dfrac{\bar{C}_p^{E,\infty}}{R}$	$\dfrac{A}{R}$	B
D2EEP	n-Heptane	5.25	2064.30	−36.28
	1-Heptene	2.43	1032.40	−16.99
	Methylcyclohexane	3.14	1311.50	−22.10
	Toluene	3.63	1396.01	−25.65
DIDP	n-Heptane	5.70	2332.81	−40.01
	1-Heptene	5.26	2148.83	−37.02
	Methylcyclohexane	4.61	1961.50	−32.77
	Toluene	4.71	1805.94	−33.24
BBP	n-Heptane	5.40	2542.02	−37.01
	1-Heptene	4.33	1905.02	−29.88
	Methylcyclohexane	3.62	1757.30	−25.38
	Toluene	2.69	1051.20	−18.84
BEEP	n-Heptane	3.18	1294.12	−22.10
	1-Heptene	1.88	755.22	−13.13
	Methylcyclohexane	1.62	684.73	−11.55
	Toluene	2.63	1033.35	−18.81

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