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Note

The application of gas–liquid chromatography to the determination of the temperature dependence of the excess partial molar enthalpy of mixing at infinite dilution*

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The application of gas–liquid chromatography (GLC) to the determination of infinite dilution activity coefficients of volatile solutes in a solvent of low volatility is well known. The experimental results have been used by various workers both for the characterization of the solvents used as stationary phases and for the evaluation of the effect of non-ideality in the gas phase.

From experimental values of activity coefficients, one can determine $\bar{G}_i^{E,\infty}$ (excess partial molar free energy of component i at infinite dilution) and, if an interval of temperature is considered, also the excess partial molar enthalpy of mixing at infinite dilution:

$$\bar{H}_i^{E,\infty} = -RT^2 \left(\frac{\partial \ln \gamma_i^\infty}{\partial T}\right)_p \qquad (1)$$

and the excess partial molar entropy at infinite dilution, $\bar{S}_i^{E,\infty}$. Generally, the temperature interval in which a stationary phase is studied is not very large and therefore the excess partial molar enthalpy of mixing calculated by eqn. 1 is nearly constant with temperature.

In studying the behaviour of hydrocarbon solutes in glycols[1] in a temperature interval of 50 °C, we have not noticed any appreciable change in $\bar{H}_i^{E,\infty}$. In contrast, in the determination of activity coefficients of hydrocarbon solutes in phthalate esters in the temperature inverval from 25 to 125 °C, no linear relationship between ln γ_i^∞ and $1/T$ was found. We have attributed this effect, which cannot be ascribed to experimental errors, to the change in $\bar{H}_i^{E,\infty}$ with temperature.

It is thus possible to use GLC for evaluating the excess partial molar heat capacity of component i at infinite dilution[2]:

$$\bar{C}_{p_i}^{E,\infty} = \left(\frac{\partial \bar{H}_i^{E,\infty}}{\partial T}\right)_p \qquad (2)$$

The importance of the determination of this quantity, for which only few data

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have been reported, is evident; in fact, its knowledge permits the evaluation of the change in $\bar{H}_i^{E,\infty}$ with temperature.

The activity coefficients can be calculated exactly at any temperature by means of the relationship

$$\ln \gamma_i^\infty = -\frac{\bar{C}_{P_i}^{E,\infty}}{R} \cdot \ln T + \frac{A}{R} \cdot \frac{1}{T} + B \qquad (3)$$

where A and B are constants.

In this work, the values of A and B and the values of $\bar{C}_{P_i}^{E,\infty}$ for hydrocarbon solutes were calculated, so that the activity coefficients of a solute in the phthalate esters could be determined at any temperature.

TABLE I

NATURAL LOGARITHMS OF INFINITE DILUTION ACTIVITY COEFFICIENTS OF HYDROCARBONS ($\ln \gamma_i^\infty$) IN 2-ETHYLHEXYL PHTHALATE AT VARIOUS TEMPERATURES

Compound	*ln γ_i^∞*				
	Temperature (°K)				
	298	*323*	*348*	*373*	*398*
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-Hexene	0.19	0.13	0.11	0.10	0.085
1-Heptene	0.34	0.25	0.22	0.21	0.17
Cyclohexane	0.094	0.028	−0.007	−0.025	−0.040
Methylcyclohexane	0.19	0.098	0.042	0.011	−0.010
Benzene	−0.39	0.43	−0.45	−0.46	−0.46
Toluene	−0.29	−0.37	−0.40	−0.41	−0.42

TABLE II

NATURAL LOGARITHMS OF INFINITE DILUTION ACTIVITY COEFFICIENTS OF HYDROCARBONS ($\ln \gamma_i^\infty$) IN BUTYLBENZYL PHTHALATE AT VARIOUS TEMPERATURES

Compound	*ln γ_i^∞*				
	Temperature (°K)				
	298	*323*	*348*	*373*	*398*
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-Hexene	1.01	0.86	0.79	0.74	0.69
1-Heptene	1.11	1.10	0.92	0.87	0.81
Cyclohexane	1.01	0.83	0.73	0.61	0.58
Methylcyclohexane	1.12	0.96	0.84	0.78	0.69
Benzene	−0.81	−0.24	−0.26	−0.27	−0.28
Toluene	−0.011	−0.076	−0.10	−0.11	−0.12

EXPERIMENTAL

The activity coefficients of hydrocarbons in two phthalate esters were determined according to ref. 3. The various quantities appearing in the equation which gives the activity coefficients were evaluated according to refs. 3 and 4.

The GLC apparatus was a thermal conductivity chromatograph (Fractovap Model B, Carlo Erba, Milan, Italy). The solvents and solutes used were reagent-grade products obtained from Fluka (Buchs, Switzerland), Monsanto (St. Louis, Mo., U.S.A.) and Union Carbide (New York, N.Y., U.S.A.).

RESULTS AND DISCUSSION

Tables I and II give the natural logarithms of the infinite dilution activity coefficients of some hydrocarbon solutes, calculated according to refs. 3 and 4, at various temperatures in two stationary phases (2-ethylhexyl and butylbenzyl phthalate).

By using the least-squares method, the values of the constants in eqn. 3 were calculated for each solute in the two stationary phases (Tables III and IV).

TABLE III

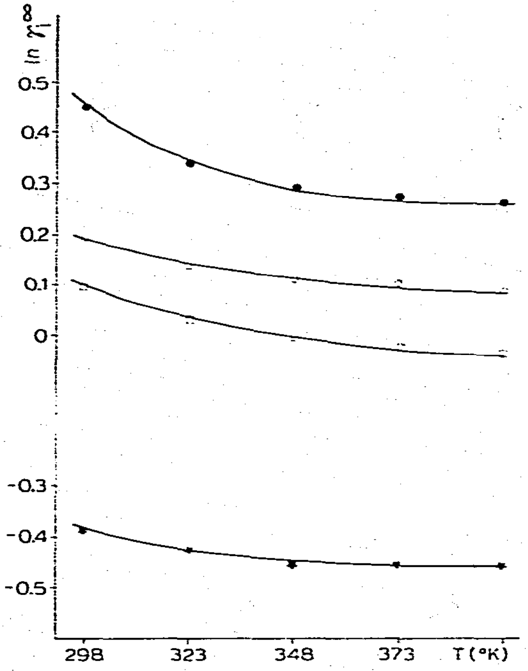
CONSTANTS OF EQN. 3 FOR HYDROCARBONS IN 2-ETHYLHEXYL PHTHALATE

Compound	$\frac{\bar{C}_{P_i}^{E,\infty}}{R}$	$\frac{A}{R}$	B
n-Pentane	4.78	1826.22	−33.00
n-Hexane	5.05	1956.60	−34.92
n-Heptane	5.25	2064.30	−36.28
n-Octane	5.54	2156.01	−38.19
1-Hexene	2.01	818.00	−13.98
1-Heptene	2.43	1032.40	−16.99
Cyclohexane	2.37	971.08	−16.65
Methylcyclohexane	3.14	1311.50	−22.10
Benzene	2.27	863.86	−16.23
Toluene	3.63	1396.01	−25.65

TABLE IV

CONSTANTS OF EQN. 3 FOR HYDROCARBONS IN BUTYLBENZYL PHTHALATE

Compound	$\frac{\bar{C}_{P_i}^{E,\infty}}{R}$	$\frac{A}{R}$	B
n-Pentane	4.90	2252.73	−34.15
n-Hexane	5.15	2402.93	−35.91
n-Heptane	5.40	2542.02	−37.01
n-Octane	5.64	2724.80	−39.48
1-Hexene	3.62	1617.70	−25.05
1-Heptene	4.33	1905.02	−29.88
Cyclohexane	3.15	1593.14	−22.25
Methylcyclohexane	3.62	1757.30	−25.38
Benzene	2.13	839.72	−15.15
Toluene	2.69	1051.20	−18.84



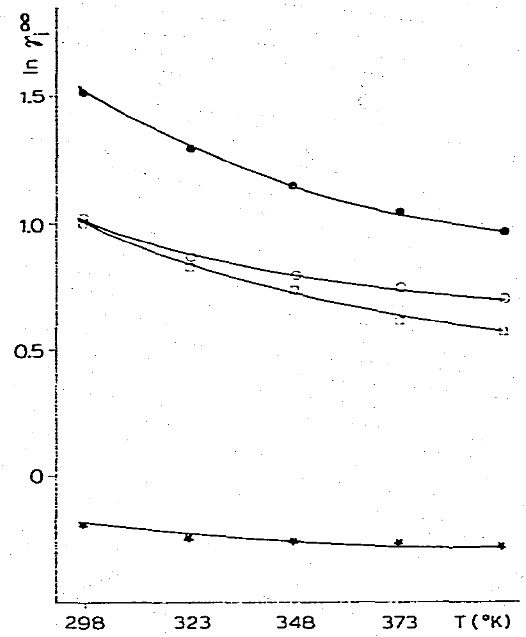


Fig. 1. Comparison between experimental and calculated values (eqn. 3) of ln γ_i^∞ in 2-ethylhexyl phthalate. ●, *n*-Hexane; ○, 1-hexene; □, cyclohexane; ★, benzene.

Fig. 2. Comparison between experimental and calculated values (eqn. 3) of ln γ_i^∞ in butylbenzyl phthalate. Symbols as in Fig. 1.

In support of the validity of the correlation, Figs. 1 and 2 show, as examples, the experimental activity coefficients of hydrocarbons with six carbon atoms, at various temperatures, and the curve of eqn. 3 obtained using the parameters in Tables III and IV. All the $\bar{C}_{p_i}^{E,\infty}$ values are negative and about 10 cal/mole·°K.

In the homologous series of *n*-paraffins, $\bar{C}_{p_i}^{E,\infty}$ increases in absolute value with increasing molecular weight of the solute. A similar variation is also found for aromatic hydrocarbons, olefins and cycloparaffins.

When the type of solute is changed, in butylbenzyl phthalate as stationary phase, $\bar{C}_{p_i}^{E,\infty}$ increases in absolute value on passing from aromatic hydrocarbons, through cycloparaffins and olefins, to paraffins, while in 2-ethylhexyl phthalate, the olefins have the lowest $\bar{C}_{p_i}^{E,\infty}$ values. The other two constants also show a regular variation with the molecular weight and the nature of the solute.

The effect of the nature of the stationary phase on $\bar{C}_{p_i}^{E,\infty}$ will also be investigated on a larger number of phthalate esters, and the results will be published in a subsequent paper.

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