CORRELATION BETWEEN THE STRUCTURE OF THE STATIONARY PHASE AND ACTIVITY COEFFICIENTS IN GAS-LIQUID CHROMATOGRAPHY

BEHAVIOUR OF SOME PARAFFINS AND CYCLOHEXANIC HYDROCARBONS ON THE ESTERS OF PHTHALIC ACID AND OTHER SIMILAR PHASES

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(Received February 28th, 1969)

SUMMARY

The present work examines the relationship between the structure of the stationary phase and activity coefficients in gas-liquid chromatography.

Twenty-five esters of benzenedicarboxylic acids, or their isomers, and other similar compounds were chosen for study as liquid stationary phases, while paraffins and cyclohexanic hydrocarbons were used as solutes. On the basis of the experimental data obtained, some speculations are made about the possible character of the intermolecular forces between solute and solvent. It is thought that some of the results might be useful in the selection of liquid phases.

INTRODUCTION

As has been shown previously[1,2], gas-liquid chromatography can be used to obtain data on the thermodynamics of infinitely diluted solutions. Such data are connected with the problem of solute-solvent interactions and provide a basis for the selection of liquid phases in analytical gas-liquid chromatography. In our previous papers[3,4], we reported the influence of the structure of phthalic acid esters on the activity coefficients of some aromatic hydrocarbons. It was found that the activity coefficients decrease with increasing number of carbon atoms in the alcohol alkyl groups.

The present study is an attempt to ascertain the influence of the structures of the esters mentioned above on the activity coefficients of some paraffins and cyclohexanes in order to establish more completely the relationship between the structure of the stationary phases and their behaviour, from a thermodynamic point of view, in gas-liquid chromatography.

The activity coefficients, γ, are related to retention volumes in gas-liquid chromatography according to the well-known expression:

$$\gamma = \frac{RT}{M \cdot P \cdot V_g{}^t} \tag{1}$$

where R is the gas constant per mole, T is the column temperature in °K, M is the molecular weight of the stationary phase, P is the vapour pressure of the pure solute, and $V_g{}^t$ is the retention volume (measured from the air peak, then corrected for compressibility) per gram of solvent at column temperature.

EXPERIMENTAL

Retention volumes were measured with a "Fractovap" Model B apparatus. The detector, together with the chromatographic column, was enclosed in an air thermostat, with the temperature controlled to $\pm 0.1°$ C. Pure dry nitrogen was used as the carrier gas, at a flow rate of 120 ml/min. The outlet of the column was under atmospheric pressure, corrected for water vapour pressure in the soap flow meter. The stainless steel column was 2 m × 6 mm (I.D.).

The column was packed with ground unglazed tile (particle diam., 0.2–0.4 mm), with stationary phase amounting to 17.6 % (w/w) of the inert support.

Retention volumes were corrected for the amount which evaporated from the column stationary phase. All the phases were studied at 120° C. The hydrocarbons employed as solutes were n-hexane, n-heptane, n-octane, n-nonane, 2,2,4-trimethylhexane, 2,3,3-trimethylhexane, cyclohexane, cyclohexene, methylcyclohexane, ethylcyclohexane, cis-1,2-dimethylcyclohexane and trans-1,2-dimethylcyclohexane. The vapour pressures of the pure hydrocarbons investigated were calculated from reference data[5,6]. Samples of 0.001 ml were used, since this amount gives only a negligible error in retention volume values and obviates the need of extrapolation to zero sample size.

All the esters investigated as stationary phases, with the exception of dinonyl phthalate, were synthesized by the authors. They were: di-n-propyl phthalate, di-isopropyl phthalate, diallyl phthalate, di-n-butyl phthalate, di-sec.-butyl phthalate, diisobutyl phthalate, di-n-hexyl phthalate, di-n-octyl phthalate, di-n-decyl phthalate, diphenyl phthalate, dibenzyl phthalate, di-(β-phenylethyl) phthalate, di-(γ-phenylpropyl) phthalate, di-n-hexyl isophthalate, di-n-hexyl terephthalate, catechol dibutyrate, catechol dibenzoate, di-n-butylphthalyl-bis-glycolate, dicyclohexyl phthalate, dibornyl phthalate, di-n-hexyl 4-nitrophthalate, di-n-butyl tetrachlorophthalate, dinonyl phthalate, di-n-hexyl adipate and di-n-hexyl suberate.

RESULTS AND DISCUSSION

The retention volumes of the paraffins and cyclohexanes per gram of solvent at 120° C are shown in Tables I and II. It is evident from the data that the increase of the number of $-CH_2-$ groups in the alcoholic alkyl chains of the di-n-alkyl and di-ω-phenylalkyl phthalates leads to an increase in the retention volume values of the hydrocarbons being investigated. This increase is practically linear if the stationary phases are di-ω-phenylalkyl phthalates. With di-n-alkyl phthalates the dependence becomes nonlinear at molecular weights higher than 400.

TABLE I

RETENTION VOLUMES, $V_g{}^t$, OF PARAFFINS AT 120° C

| No.	Phase	Hydrocarbon					
		n-Hexane	n-Hep-tane	n-Octane	n-Nonane	Trimethylhexane	
						2,2,4	2,3,3
1	Di-n-propyl phthalate	13.0	28.2	52.2	97.5	50.6	73.0
2	Di-n-butyl phthalate	14.1	28.9	54.2	102.3	52.7	78.4
3	Di-n-hexyl phthalate	15.1	32.4	62.4	118.2	60.8	89.1
4	Di-n-octyl phthalate	16.5	34.8	68.8	131.7	67.5	99.4
5	Di-n-decyl phthalate	17.0	35.6	69.2	135.2	66.2	96.8
6	Diphenyl phthalate	5.8	11.5	20.2	36.0	17.3	28.4
7	Dibenzyl phthalate	6.6	11.9	22.1	39.6	20.0	31.5
8	Di-(β-phenylethyl) phthalate	7.5	12.6	22.8	41.7	19.6	32.3
9	Di-(γ-phenylpropyl) phthalate	8.2	13.6	25.3	54.8	22.5	36.6
10	Diisopropyl phthalate	13.5	26.8	51.5	96.8	50.6	74.4
11	Diallyl phthalate	9.1	19.1	35.6	65.0	33.5	60.0
12	Di-sec.-butyl phthalate	14.4	28.9	53.9	101.7	53.4	78.4
13	Diisobutyl phthalate	14.6	29.2	52.5	102.4	50.8	79.0
14	Dinonyl phthalate	16.6	35.8	69.6	132.2	66.6	99.9
15	Di-n-hexyl isophthalate	18.8	38.6	75.5	145.6	72.9	111.0
16	Di-n-hexyl terephthalate	19.5	39.1	77.1	144.7	75.2	111.6
17	Dicyclohexyl phthalate	9.9	20.8	42.0	80.4	36.9	59.6
18	Dibornyl phthalate	6.5	15.4	40.2	86.1	27.8	47.9
19	Catechol dibutyrate	12.7	23.4	44.5	81.5	42.8	63.4
20	Catechol dibenzoate	7.0	12.2	23.5	41.5	19.6	31.4
21	Di-n-hexyl 4-nitrophthalate	13.2	25.7	48.2	93.3	48.6	72.4
22	Di-n-butyl tetrachlorophthalate	13.2	26.4	51.4	99.0	52.8	80.0
23	Di-n-butylphthalyl-bis-glycolate	8.5	15.6	32.5	50.5	27.6	41.2
24	Di-n-hexyl adipate	22.0	43.9	84.9	166.0	84.3	122.1
25	Di-n-hexyl suberate	21.6	43.3	85.1	167.0	84.4	123.3
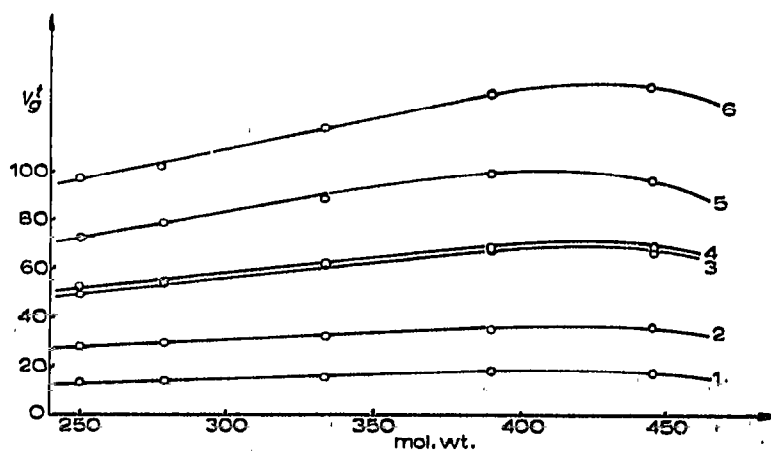
Fig. 1. Plot of the retention volumes of (1) n-hexane, (2) n-heptane, (3) 2,2,4-trimethylhexane, (4) n-octane, (5) 2,3,3-trimethylhexane, and (6) n-nonane on di-n-alkyl phthalates at 120° C vs. molecular weight of the ester.
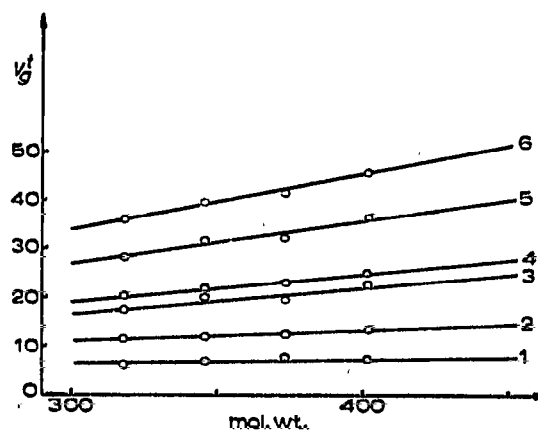
Fig. 2. Plot of the retention volumes of (1) n-hexane, (2) n-heptane, (3) 2,2,4-trimethylhexane, (4) n-octane, (5) 2,3,3-trimethylhexane, and (6) n-nonane on di-ω-phenylalkyl phthalates at 120° C vs. molecular weight of the ester.

TABLE II

RETENTION VOLUMES, $V_g{}^t$, OF CYCLOHEXANES AT 120° C

No.	Phase	Hydrocarbon					
		Cyclo-hexane	Cyclo-hexene	Methyl-cyclo-hexane	Ethyl-cyclo-hexane	1,2-Dimethyl-cyclohexane	
						Cis	Trans
1	Di-n-propyl phthalate	25.9	34.9	42.3	82.9	83.7	67.2
2	Di-n-butyl phthalate	27.7	35.8	42.9	85.8	85.0	69.4
3	Di-n-hexyl phthalate	29.0	36.6	44.4	95.8	95.4	77.3
4	Di-n-octyl phthalate	30.7	38.6	53.6	108.0	107.0	87.4
5	Di-n-decyl phthalate	32.3	38.7	51.9	105.6	104.1	86.0
6	Diphenyl phthalate	13.7	20.9	19.8	38.3	38.7	29.2
7	Dibenzyl phthalate	14.2	21.0	21.0	40.0	40.0	30.6
8	Di-(β-phenylethyl) phthalate	15.3	22.1	19.4	42.6	42.6	33.1
9	Di-(γ-phenylpropyl) phthalate	15.7	23.3	23.3	46.6	47.1	37.0
10	Diisopropyl phthalate	25.9	34.6	41.1	84.8	84.8	67.9
11	Diallyl phthalate	20.7	28.3	30.6	60.4	61.7	49.3
12	Di-sec.-butyl phthalate	26.9	34.6	44.0	86.2	86.2	69.8
13	Diisobutyl phthalate	25.1	35.2	43.3	86.6	86.6	69.6
14	Dinonyl phthalate	28.5	40.2	50.0	102.2	102.2	83.4
15	Di-n-hexyl isophthalate	34.4	43.8	53.2	113.2	113.2	93.4
16	Di-n-hexyl terephthalate	34.7	43.4	55.4	115.0	112.8	95.4
17	Dicyclohexyl phthalate	22.2	31.3	35.0	71.5	70.4	55.8
18	Dibornyl phthalate	13.1	20.6	23.2	58.8	56.4	42.5
19	Catechol dibutyrate	23.9	32.1	34.6	69.2	69.2	56.0
20	Catechol dibenzoate	13.6	21.8	20.5	40.6	41.0	32.3
21	Di-n-hexyl 4-nitrophthalate	24.5	33.1	38.9	77.8	77.8	64.6
22	Di-n-butyl tetrachlorophthalate	25.7	34.8	41.8	85.8	87.0	72.6
23	Di-n-butylphthalyl-bis-glycolate	17.1	24.9	25.7	49.4	49.4	39.6
24	Di-n-hexyl adipate	39.2	48.7	61.2	125.5	122.8	100.9
25	Di-n-hexyl suberate	39.6	48.8	62.8	127.3	132.6	103.0

Figs. 1 and 2 show graphically the relationship $V_g{}^t = $ f (mol. wt.) for some paraffinic hydrocarbons on di-n-alkyl and di-ω-phenylalkyl phthalates. It can be seen that when the molecular weight of the phase is the same, the retention volumes are lower on the di-ω-phenylalkyl phthalates than on the di-n-alkyl phthalates.

If we compare the retention volumes on di-n-propyl and on diallyl phthalate, it can be seen that the presence of double bonds in the side chains of the ester decreases these values. Such a decrease also appears when saturated or aromatic rings are present in the side chains of the ester, as in the case of di-n-hexyl, dicyclohexyl and diphenyl phthalates. On diphenyl phthalate, for example, the retention volumes are smaller than on the other two esters mentioned above.

The influence of the ring structures can also be seen if one compares the data for di-n-hexyl adipate, di-n-hexyl suberate and di-n-hexyl terephthalate. Di-n-hexyl adipate has the same number of C atoms between the two carboxy groups, and di-n-hexyl suberate has the same total number of C atoms as the terephthalic ester. The retention volumes are higher on the esters of the aliphatic dicarboxylic acids than on the ester with the phthalic ring.

If we compare the retention volumes of the solutes on the esters of isomeric benzenedicarboxylic acids, it may be seen that they are lowest on di-n-hexyl phthalate and higher, but almost the same, on di-n-hexyl iso- and terephthalates.

TABLE III

ACTIVITY COEFFICIENTS, γ, OF PARAFFINS AT 120° C

No.	Phase	Hydrocarbon				Trimethylhexane	
		n-Hexane	n-Heptane	n-Octane	n-Nonane	2,2,4	2,3,3
I	Di-n-propyl phthalate	2.52	2.53	2.90	3.21	3.06	2.91
2	Di-n-butyl phthalate	2.09	2.22	2.51	2.75	2.64	2.44
3	Di-n-hexyl phthalate	1.63	1.65	1.82	1.98	1.91	1.79
4	Di-n-octyl phthalate	1.27	1.32	1.41	1.52	1.47	1.37
5	Di-n-decyl phthalate	1.08	1.12	1.23	1.30	1.31	1.23
6	Diphenyl phthalate	4.44	4.88	5.90	6.82	7.02	5.88
7	Dibenzyl phthalate	3.59	4.34	4.95	5.70	5.59	4.88
8	Di-(β-phenylethyl) phthalate	2.92	3.79	4.44	5.00	5.28	4.40
9	Di-(γ-phenylpropyl) phthalate	2.49	3.27	3.72	4.24	4.28	3.61
10	Diisopropyl phthalate	2.43	2.66	2.94	3.23	3.06	2.86
11	Diallyl phthalate	3.66	3.80	4.32	4.88	4.70	3.60
12	Di-sec.-butyl phthalate	2.05	2.22	2.55	2.76	2.65	2.47
13	Diisobutyl phthalate	2.02	2.20	2.59	2.74	2.74	2.44
14	Dinonyl phthalate	1.18	1.19	1.30	1.41	1.39	1.27
15	Di-n-hexyl isophthalate	1.31	1.38	1.50	1.61	1.59	1.43
16	Di-n-hexyl terephthalate	1.26	1.37	1.47	1.62	1.54	1.43
17	Dicyclohexyl phthalate	2.51	2.60	2.73	2.94	3.18	2.70
18	Dibornyl phthalate	2.88	2.65	2.15	2.07	3.18	2.53
19	Catechol dibutyrate	2.58	3.05	3.40	3.83	3.62	3.35
20	Catechol dibenzoate	3.68	4.61	5.07	5.92	6.21	5.32
21	Di-n-hexyl 4-nitrophthalate	1.65	1.83	2.07	2.21	2.12	1.94
22	Di-n-butyl tetrachlorophthalate	1.49	1.63	1.77	1.90	1.76	1.60
23	Di-n-butylphthalyl-bis-glycolate	2.45	2.90	2.95	3.92	3.47	3.27
24	Di-n-hexyl adipate	1.19	1.29	1.42	1.50	1.46	1.39
25	Di-n-hexyl suberate	1.11	1.21	1.30	1.37	1.34	1.26

The activity coefficients of the solutes dissolved in the stationary phases studied at 120° C are given in Tables III and IV. The activity coefficients of the paraffins and cyclohexanes decrease with increasing numbers of $-CH_2-$ groups in the alcohol alkyl chains of the ester. When the ester is a di-n-alkyl phthalate, the decrease is not linear as it is when the ester is a di-ω-phenylalkyl phthalate.
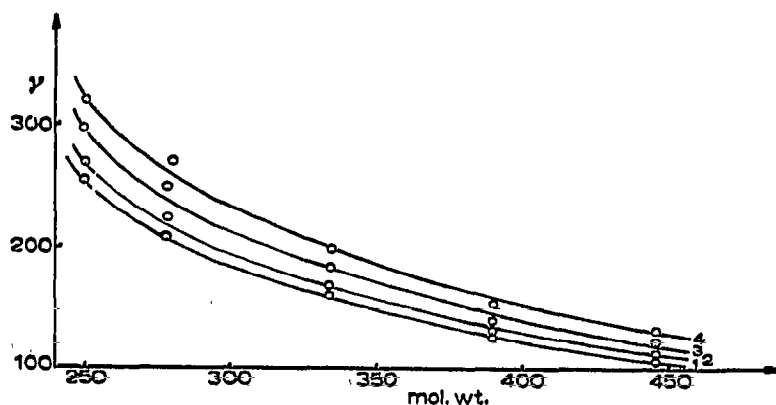
The changes in the activity coefficients of the paraffins and cyclohexanes which depend on the molecular weight of the di-n-alkyl and di-ω-phenylalkyl phthalates, are shown graphically in Figs. 3 and 4. It may be seen from Tables III and IV and from the figures that lengthening the alcohol alkyl chains brings the solution close to the ideal state ($\gamma = 1$). This change of the activity coefficients is probably due to two factors. In the first place it can be assumed that dispersion forces are present between the molecules of the hydrocarbon and of the ester. These forces decrease rapidly with increasing distance between the molecules and are strongest if the molecules are in direct contact. The accumulation of methylene groups in the molecule of the phthalic ester provides an opportunity for a greater number of contacts with the methylene groups of the hydrocarbons.

On the other hand, the second factor influencing the activity coefficients is the mutual accessibility of the interacting molecules. In this respect it can be mentioned that the activity coefficients of the alkanes do not reach a value close to unity when

TABLE IV

ACTIVITY COEFFICIENTS, γ, OF CYCLOHEXANES AT 120° C

No.	Phase	Hydrocarbon					
		Cyclo-hexane	Cyclo-hexene	Methyl-cyclo-hexane	Ethyl-cyclo-hexane	1,2-Dimethyl-cyclohexane	
						Cis	Trans
1	Di-n-propyl phthalate	1.63	1.37	1.79	2.17	2.03	2.11
2	Di-n-butyl phthalate	1.37	1.20	1.59	1.89	1.80	1.84
3	Di-n-hexyl phthalate	1.09	0.98	1.28	1.41	1.33	1.37
4	Di-n-octyl phthalate	0.88	0.82	0.96	1.07	1.02	1.04
5	Di-n-decyl phthalate	0.73	0.69	0.82	0.96	0.91	0.92
6	Diphenyl phthalate	2.43	1.80	3.01	3.70	3.45	3.82
7	Dibenzyl phthalate	2.16	1.65	2.61	3.26	3.05	3.34
8	Di-(β-phenylethyl) phthalate	1.85	1.45	2.34	2.83	2.66	2.86
9	Di-(γ-phenylpropyl) phthalate · ·	1.68	1.28	2.02	2.41	2.23	2.38
10	Diisopropyl phthalate	1.63	1.39	1.85	2.13	2.00	2.09
11	Diallyl phthalate	2.08	1.72	2.52	3.03	2.80	2.92
12	Di-sec.-butyl phthalate	1.42	1.24	1.55	1.88	1.77	1.83
13	Diisobutyl phthalate	1.52	1.22	1.57	1.87	1.76	1.83
14	Dinonyl phthalate	0.89	0.71	0.91	1.05	0.99	1.02
15	Di-n-hexyl isophthalate	0.92	0.82	1.07	1.19	1.12	1.14
16	Di-n-hexyl terephthalate	0.91	0.82	1.02	1.17	1.13	1.11
17	Dicyclohexyl phthalate	1.45	1.16	1.64	1.91	1.83	1.93
18	Dibornyl phthalate	1.85	1.33	1.87	1.75	1.72	1.90
19	Catechol dibutyrate	1.77	1.49	2.19	2.60	2.45	2.53
20	Catechol dibenzoate	2.45	1.73	2.91	3.41	3.26	3.45
21	Di-n-hexyl 4-nitrophthalate	1.14	0.95	1.29	1.53	1.44	1.45
22	Di-n-butyl tetrachlorophthalate	0.99	0.83	1.09	1.26	1.17	1.17
23	Di-n-butylphthalyl-bis-glycolate	1.57	1.22	1.87	2.32	2.18	2.27
24	Di-n-hexyl adipate	0.86	0.78	0.99	1.14	1.10	1.12
25	Di-n-hexyl suberate	0.78	0.72	0.88	1.04	0.94	1.01

Fig. 3. Dependence of the activity coefficients of (1) n-hexane, (2) n-heptane, (3) n-octane, and (4) n-nonane at 120° C on the molecular weight of the di-n-alkyl phthalate used.

the alcohol alkyl chain and that of the hydrocarbon have an equal number of methylene groups. This could be explained by assuming that the phthalic group causes steric hindrance, making a lower number of methylene groups of the ester accessible.

It is also of interest that the activity coefficients of a given alkane on di-n-alkyl phthalate and on di-ω-phenylalkyl phthalate, which have very similar molecular

weights, are quite different. This difference, however, is negligible if we compare the activity coefficients of esters having an equal number of methylene groups in the side chains (*e.g.* di-*n*-propyl phthalate and di-γ-phenylpropyl phthalate). For a given hydrocarbon, the influence of the accumulation of methylene groups in the alcohol alkyl chains should end when the chain reaches a certain length. This assumption is in accordance with experimental facts; for example the activity coefficients of the hydrocarbons listed in Fig. 3 tend toward unity.
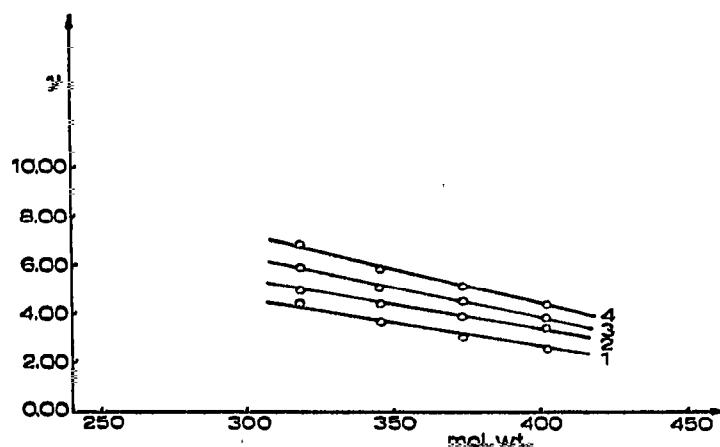
Fig. 4. Dependence of the activity coefficients of (1) *n*-hexane, (2) *n*-heptane, (3) *n*-octane, and (4) *n*-nonane at 120° C on the molecular weight of the di-ω-phenylalkyl phthalate used.
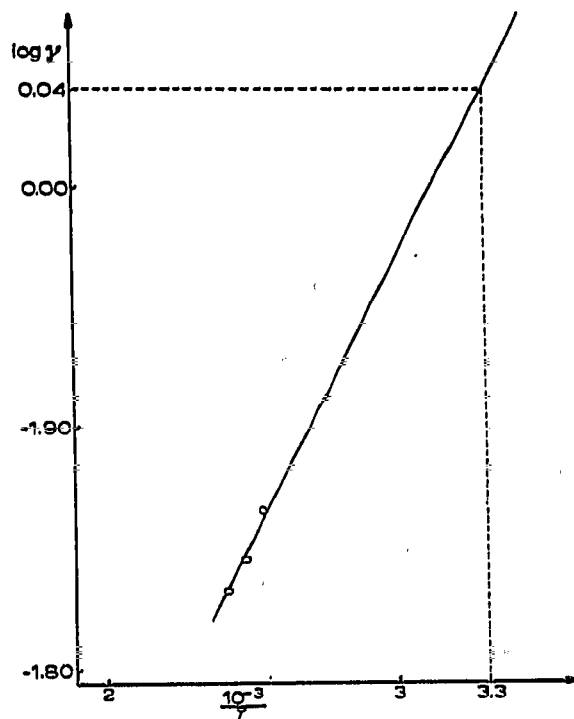
Fig. 5. Plot of the activity coefficient of cyclohexane/di-*n*-decyl phthalate *vs.* the reciprocal of the temperature.

It is interesting, however, that after reaching unity, the values of the activity coefficients gradually fall in the region of the negative deviations from Raoult's law.

This could be explained by the fact that, with lengthening of the carbon chains in the ester, the difference between the molecular sizes of the solute and of the solvent becomes greater.

The main forces between the cyclohexanes and the esters investigated are probably dispersion forces, too. For example, extrapolating from the values of the activity coefficients of cyclohexane on di-*n*-decyl phthalate at 120, 130 and 140° C (0.73, 0.70 and 0.68, resp.), a value of 1.01 is found at 30° C (Fig. 5). The activity coefficient of cyclohexane on *n*-decane (in this case only dispersion forces are possible) at the same temperature is 0.94 (ref. 7). These two values are in good agreement considering the error of the extrapolation. It might be thought, therefore, that the interaction forces are similar in these two cases.

Investigation of the activity coefficients of hydrocarbons on di-n-hexyl, dicyclohexyl and diphenyl phthalates shows that their values increase in the order mentioned above, $i.e.$ the cohesion forces are strongest when the alcohol chains are linear and weaker when a ring structure is present. The lowest values are obtained when the ring is aromatic. The activity coefficients of di-n-propyl phthalate and diallyl phthalate show that greater positive deviations from Raoult's law appear with the latter phase, probably due to the presence of a double bond in the alcohol alkyl group.

It is the authors' opinion that the steric position of the π-orbitals diminishes the possibility of contact between the molecules of the solute and solvent. It is interesting to note that the accumulation of double bonds in the solute molecule increases the interaction with the liquid phase. For instance, the activity coefficients of cyclohexane, cyclohexene and benzene (see ref. 3) decrease on the same stationary phase, depending on the number of double bonds in their molecules.

If the properties of the esters of phthalic, isophthalic and terephthalic acids are compared it is found that the activity coefficients of the paraffins and cyclohexanes show the highest values on di-n-hexyl phthalate and the lowest on di-n-hexyl terephthalate. The linear molecule of the terephthalic ester probably provides a better opportunity for the solvent molecules to be closely arranged around the solute molecules. The activity coefficients of esters obtained on di-n-butyl phthalate and on di-n-butylphthalyl-bis-glycolate increase with increasing number of carboxyl groups. This is probably due to steric factors. Compared with di-n-butyl phthalate, di-n-butyl tetrachlorophthalate is a solvent which gives fewer positive deviations from Raoult's law. The tetrachlorophthalic acid ester system has more electrons, a condition for the presence of stronger dispersion forces.

In conclusion the data in Tables III and IV show that the activity coefficients of the solutes studied on di-n-hexyl terephthalate, di-n-hexyl adipate and di-n-hexyl suberate are similar. However, the molecular interactions are stronger on the second and the third esters. The linear carbon chain of the aliphatic dicarboxylic acid probably provides better steric opportunities for contacts and, therefore, stronger dispersion forces than the structure of the terephthalic ester.

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