in the α-functions. The error in α_{Au} appears to be about ± 0.01 unit in the region $X_{Cu} = 0$ to $X_{Cu} = 0.4$ and to vary approximately linearly thereafter to ± 0.02 unit at $X_{Cu} = 1$. The error in α_{Cu} appears to be ± 0.01 unit from $X_{Cu} = 0$ to about $X_{Cu} = 0.7$ and to vary approximately linearly thereafter to ± 0.05 unit at $X_{Cu} = 1$, if the nature of the extrapolation has been correctly assumed.

The molar enthalpy of mixing is found to be $-2{,}720 \pm 200$ cal. at $X_{Cu} = 0.5$ which is about 800 cal. more negative than Oriani reported and considerably more negative than the calorimetric value of zero which Kawakami[12] obtained. The general agreement of our work with that of Oriani leads us to discount the calorimetric value. The partial molar enthalpy of mixing of Cu for the solutions infinitely dilute in Cu is found to be $-10{,}800 \pm 700$ cal. The partial molar enthalpy of Au for the solutions infinitely dilute in Au is found to be $-7{,}290 \pm 700$ cal.

[12] M. Kawakami, *Sci. Rep. Tohoku. Imp. Univ.*, **19**, 521 (1930).

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Solvent Effects in Gas–Liquid Partition Chromatography

BY G. J. PIEROTTI, C. H. DEAL, E. L. DERR AND P. E. PORTER

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For the purpose of considering solvent effects in GLPC, the partition coefficient (H^0) is discussed in terms of the vapor pressure of the solute (P^0) and the thermodynamically defined activity coefficient of solute in the solvent (γ^0). This separation of effects leads to a clear understanding of the interrelations of solute and solvent behavior in GLPC operations and provides the basis for exploiting relations which have been found in direct studies of solutions. This in turn leads to a number of observations which are useful in practical GLPC work. The more important of these are: (1) At a given temperature and within an homologous series of solutes the logarithm of the ratio of partition coefficients in solvents may be expected to be a linear function of the solute carbon number. The slopes of such plots for different homologous series may be expected to be the same. (2) Over the restricted ranges in carbon number of interest in a given GLPC separation and except for the first several members of an homologous series, log H^0 for the members of an homologous series may be expected to be linear in carbon number. This observation is closely related to ones already appearing in the literature.

James, Martin and other workers in the field[1–5] have discussed solvent effects in gas–liquid partition chromatographic (GLPC) separations in terms of the fundamental nature of the solute–solvent interactions which occur in the liquid phase and in terms of regularities in GLPC behavior observed among the members of homologous series. A companion paper[6] to the present one has shown that the solvent supports usually used are substantially inert and that GLPC behavior can be largely accounted for in terms of the deviations from ideal behavior in the bulk liquid phase. It is the purpose of the present paper to discuss GLPC solvent effects in more empirical but more quantitative terms than hitherto has been done, exploiting for this purpose observations drawn from direct studies of the non-ideal behavior of solutions.

In the present paper the partition coefficients which characterize GLPC behavior are considered in terms of fundamental solution parameters. Useful and generally applicable relations between solute activity coefficients and structural groupings of solute and solvent are outlined. These are applied in order to illustrate the interplay of solute and solvent properties in setting GLPC behavior in several cases. Useful methods of treating GLPC data are outlined and illustrated.

Experimental

Partition coefficients from GLPC measurements have been determined as described in the previous paper for a number of additional solutes in the two solvents, diisodecyl phthalate and squalane, and in a more polar solvent, Triol. Partition coefficients are shown in Table I; for completeness some of the data presented in the previous paper have been repeated.

Discussion

GLPC Partition Coefficients and Fundamental Solute–Solvent Parameters.—As indicated in the previous paper,[6] the partition coefficient determined from GLPC data is essentially that operative when the solute is at infinite dilution in the solvent phase. In terms of fundamental parameters of the solute and solvent, this may be expressed as

$$H^0 = \frac{M_s RT}{\gamma^0 P^0} \tag{I}$$

where M_s is the reciprocal molar volume of the solvent, γ^0 is the activity coefficient of the solute at infinite dilution in the solvent, P^0 is the vapor pressure of the solute and RT has its usual meaning. Equation I leads directly to an expression for the relative partition coefficients of two solute materials, 2 and 1, or to the relative volatility of solute 1 to solute 2, at infinite dilution in the solvent

$$\alpha_{1,2} = \frac{H_2^0}{H_1^0} = \frac{\gamma_1^0 P_1^0}{\gamma_2^0 P_2^0} \tag{II}$$

This is identical with the separation coefficient normally used to measure the ease of separation of two components by distillation. Although the number of plates in a column of given geometry varies from solvent to solvent as a result of differ-

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[1] A. T. James and A. J. P. Martin, *Biochem. J.*, **50**, 679 (1952).

[2] A. T. James and A. J. P. Martin, *British Med. Bull.*, **10**, 170 (1954).

[3] A. T. James, A. J. P. Martin and G. Howard-Smith, *Biochem. J.*, **52**, 238 (1952).

[4] A. J. P. Martin and R. L. M. Synge, *ibid.*, **50**, 532 (1943).

[5] A. J. P. Martin, Biochem. Soc. Symposia No. 3, 4 (1951).

[6] P. E. Porter, C. H. Deal and F. H. Stross, THIS JOURNAL, **78**, 2999 (1956).

TABLE I

AVERAGE PARTITION COEFFICIENTS FROM GLPC MEASUREMENTS

Solute	Solvent Diisodecyl phthalate	"Triol"[a]	Squalane[b]
n-Pentane			16.3
n-Hexane	27.0	11.0	34.8
n-Heptane	57.6	21.0	72.9
n-Octane	121	30.4	
n-Nonane	240	56.4	
2,2-Dimethylbutane	19.5		
2,4-Dimethylpentane	35.2		
2,3-Dimethylhexane	73.3		
2,4-Dimethylhexane	89.7		
2,2,5-Trimethylhexane	93.9		
Methylcyclopentane	38.2		
Cyclohexane	52.3		60.1
Methylcyclohexane	(83.5)		97.4
Ethylcyclohexane	(180)		
1-Hexene	26.9	10.5	
2-Heptene	64.6	18.9	
1-Octene	119	27.5	
Toluene	144		
Methanol	12.6		
Ethanol	20.9	82.5	
1-Propanol	46.2	138	
1-Butanol	107	264	
2-Propanol	26.1	81.5	
2-Butanol	77.4	173	
2-Methyl-2-butanol	73.5	128	
3-Methyl-2-butanol	105		
2-Methyl-1-butanol	154		
3-Methyl-1-butanol	161		
2-Methyl-2-propanol	30.8	72.5	
2-Methyl-1-pentanol	317		
2-Methyl-2-pentanol	188		
4-Methyl-2-pentanol	180		
3-Methyl-3-pentanol	142		
2-Hexanol	241		
3-Hexanol	239		
Acetone	19.7	32.2	
2-Butanone	42.5	52.4	
3-Pentanone	91	86.1	
3-Methyl-2-butanone	69.5		

[a] Triol is a product of Union Carbide and Carbon Co. which is 2,4-dimethyl-2-(2-hydroxyethoxy)-pentane-1,5-diol.

[b] Squalane is 2,6,10,15,19,23-hexamethyltetracosane.

ences in the physical properties of solvents, generally the magnitudes of the partition coefficients, which largely determine plate capacities, and the relative volatilities of components being separated, which determine the relative rates of band movement, are the most important quantities affecting separation.

Before proceeding to a detailed discussion of solvent effects, several general observations regarding the above quantities may be noted explicitly.

(1) M_s is purely a solvent property. Although its magnitude affects GLPC separation through the magnitudes of the partition coefficients, it is clear from II that it is not this solvent property that directly affects relative volatilities. The variation of M_s with temperature is negligible in comparison to other temperature effects.

(2) P^0 is purely a solute property. It affects GLPC separation through its effect on the magnitude of partition coefficients and through its effect on relative volatilities. For a given set of solute components to be separated, however, relative volatilities are fixed insofar as P^0 effects are concerned. P^0 is generally the most strongly temperature dependent of the above quantities, and changes in temperature strongly affect the magnitudes of partition coefficients through P^0. Relative volatilities are not as strongly affected by changes in temperature insofar as P^0 effects are concerned because the heats of vaporization of solutes are frequently roughly comparable.

(3) γ^0 is the property of solute and solvent in terms of which solvent effects can be properly expressed. This quantity affects separation both through the magnitude of partition coefficients and through relative volatilities. With a given set of solutes for separation, it is only by changes in γ^0's brought about by changes in solvent that large changes in relative volatilities of the solutes can be made. γ^0 is not as temperature dependent as P^0, and relative volatilities are usually even less temperature dependent insofar as γ^0 effects are concerned. As a result, unfavorable effects on the magnitudes of partition coefficients brought about by the use of a solvent which provides a suitably favorable relative volatility can be compensated to a large degree by changes in the temperature of operation.

In order to provide some basis for judging the magnitudes and directions of the solvent effects which may be exploited in GLPC separations, primary attention will here be given to relations between γ^0 values and the structures of solutes and solvents at a given temperature. The magnitudes of temperature effects on the quantities considered here have already been touched upon in the companion paper.[6]

Some Relations between Activity Coefficients and Structural Groupings.—The essential natures of such molecular interactions as van der Waals interactions, dipole-induced dipole, dipole–dipole, hydrogen bonding, etc., are well understood and have been discussed elsewhere.[7] Quantitative estimates of their effects on the non-idealities of solutions can be made on a fundamental basis in only a few special cases; however, qualitative ideas along these lines are useful when viewed within the framework of experimental quantitative data and have been discussed by Martin and others.[1-5]

The Scatchard–Hildebrand relation[7] permits a fairly good estimate of γ^0 for the special class of regular solutions from the energies of vaporization and molar volumes of solute and solvent. This relation is not, however, applicable to solutions in which one or both components are polar in nature, and more empirical methods must be resorted to. Pierotti, *et al.*,[8] in their direct solution studies have determined γ^0's for several hundred polar systems so chosen that the variations within homologous series of solutes and solvents can be systematically reviewed. Although many of their experimental data are not concerned with solvents of interest in

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[7] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," ACS Monograph Series, No. 17, 3rd Ed., New York, N. Y., 1950.

[8] Pierotti, *et al.*, in preparation.

GLPC separations for volatility reasons, the regularities of behavior noted are broadly applicable and can be exploited to advantage here in setting the magnitudes of solvent effects which can be achieved. Pertinent aspects of this work which is only now being prepared for publication will consequently be outlined here.

Pierotti and his co-workers have developed a semi-empirical model from experimental data which follows along lines very similar to the treatment of homologous series of Brønsted and Koefoed,[9] Butler[10] and Copp and Everett.[11] It considers the excess partial molal free energy of solution for the limiting case of solute at infinite dilution in the solvent (*i.e.*, $RT \ln \gamma^0$) as the sum of individual terms, each of which can be identified with the various characteristic groupings of the solute and/or solvent structure. The essence of the model can be most easily described as follows.

For a mono-functional solute R–X in a mono-functional solvent R′X′, where the R's are alkyl groups and X's are "functional" groups (polar groups as $-\text{OH}$ or groupings which it is convenient to consider as units as phenyl or naphthyl groups), six free energy terms associated with six net interactions of structural groupings can be imagined. These are shown in Fig. 1.

Solute: R–X
Solvent: R′X′

$$\begin{tikzcd}
R \arrow[r, leftrightarrow, "c"] \arrow[d, leftrightarrow, "d"'] \arrow[dr, leftrightarrow, "b"] & X \arrow[d, leftrightarrow, "a"] \arrow[dl, leftrightarrow, "e"] \\
R' \arrow[r, leftrightarrow, "f"'] & X'
\end{tikzcd}$$

Fig. 1.

The variations of these terms with structure within homologous series are now determined by systematic variation of the R's and X's, choosing component pairs of increasing complexity and applying the terms of each case to the next most complex case. Thus, the simplest case is R–H in R′–H, terms *a*, *b*, *c*, *e*, *f* are found to be zero or negligible, and an analytical expression for the term *d* is derived from a sufficient number of examples. Having determined an expression for the "*d*" term, the next most simple case of R–H in R′X′ is considered and so on. From such a systematic study Pierotti, *et al.*, have shown that limiting log γ can be expressed in five terms having the following forms

$$\begin{array}{l} a{:}A \\ b{:}B\ n/n' \\ c{:}C/(n + C') \\ d{:}D(n - n')^2 \\ e{:}\dots\dots\dots\dots \\ f{:}F/(n' + F') \end{array} \qquad \text{(III)}$$

where the upper case letters are constants, where n and n' are the carbon numbers of the solute and solvent, respectively, and where the e term is small or can at least be taken into account in other terms. The form of the "*d*" term is taken directly from Brønsted and Koefoed.[9] As is apparent from the way in which the structural parameters are defined above, D is a universal constant which is independent of both solute and solvent structure, C and C' are constants which are expected to be characteristic of the solute functional group and apply to an entire homologous series of solutes,[12] F, F' and B are constants which are characteristic of the solvent functional group and apply to an entire homologous series of solvents, and A is characteristic of both the solute and solvent functional group.

For the case in which the structure of a solvent is held constant and that of the solute is varied within an homologous series, n' is constant and n is variable. In this case, terms "*a*" and "*f*" are constant and in many homologous series further simplifications arise. For *n*-alkanes in polar solvents the c term does not occur and the expression for log γ^0 becomes

$$\log \gamma^0 = K_\text{p} + B(n/n') + D(n - n')^2 = K_\text{p} + B_\text{p}n + D(n - n')^2 \quad \text{(IV)}$$

where K_p includes all constant terms and B_p measures the net molecular weight effect of the polar group per methylene of the alkane, the differences between methyl and methylene groups being neglected. For *n*-alkylbenzenes the phenyl group is considered a functional group and a c term occurs. In this case the expression becomes

$$\log \gamma^0 = K_\text{AB} + B_\text{p}(n - 6) + C/(n - 4) + D(n - n')^2 \quad \text{(V)}$$

where K_AB includes all constant terms, n is the total carbon number including the phenyl group, B_p is as before, and $n-6$ measures the number of methylene plus methyl groups in the molecule.

Examples showing the magnitudes of γ^0-effects for the above "type" homologous series over a broad range of carbon number with a broad range of solvent polarities are given in Figs. 2 and 3. γ^0's are here described to within about 5% of their experimental values for representative solutes in the range up to C_{30} and there is little doubt that interpolations and extrapolations for solutes up to about C_{35} are equally accurately described. It is of particular interest that moderate branching in R or substitution on an aromatic nucleus modifies the γ^0's by only a few per cent. from the value for the corresponding straight chain or normal alkyl compound. Coefficients for the above correlations at a temperature in the temperature region frequently of interest in GLPC separations are shown in Table I. As already indicated the D coefficient is structure invarient, the B_p coefficient is solvent characteristic, the C coefficients are solute characteristic, and the K_p and K_AB are both solute type and solvent characteristic.[13]

Two factors relating to the relative solvent effects for two homologous series or "types" of solute in a given solvent will be particularly noted by the comparison shown in Fig. 4. First, except

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[9] J. N. Brønsted and J. Koefoed, *Kgl. Danske Vid. Selsk. Medd.*, **22**, 1 (1946).

[10] J. A. V. Butler, *J. Chem. Soc.*, 280 (1935).

[11] J. L. Copp and D. H. Everett, *Disc. Faraday Soc.*, 268 (1955).

[12] For the more complicated case in which the solute structure has the form R_1R_2CHX, the "*c*" term has the related form $C(1/n_1 + 1/n_2)$ where n_1 and n_2 are the carbon numbers in R_1 and R_2 increased by one.

[13] For more polar solutes the C coefficients are somewhat solvent dependent but usually are not critically so.

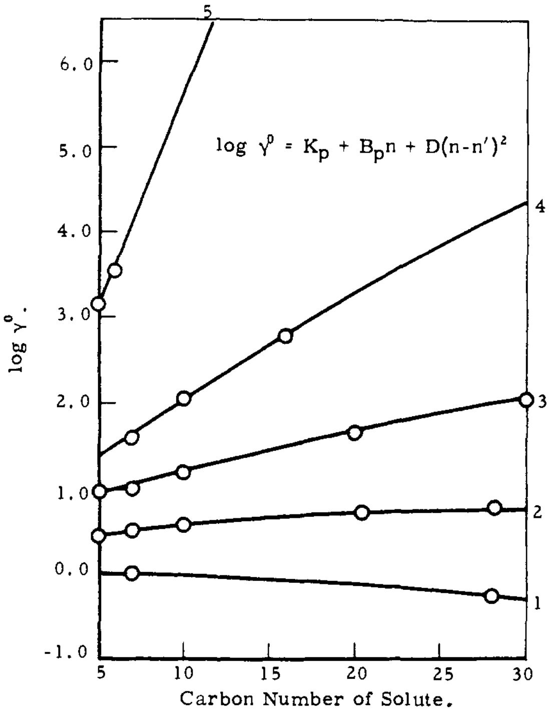

Fig. 2.—*n*-Alkanes in various solvents: solvents: 1, *n*-heptane at 90°; 2, 2-butanone at 90°; 3, phenol at 90°; 4, triethylene glycol at 90°; 5, water at 25°.

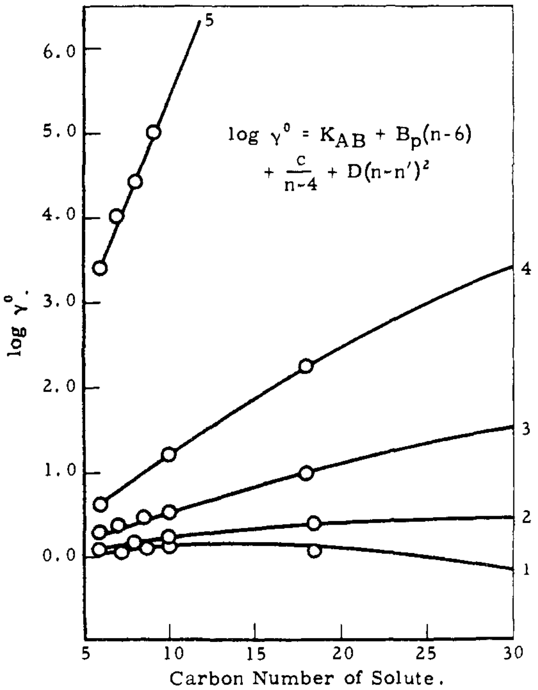

Fig. 3.—Alkylbenzenes in various solvents: solvents: 1, *n*-heptane at 90°; 2, 2-butanone at 90°; 3, phenol at 90°; 4, triethylene glycol at 90°; 5, water at 25°.

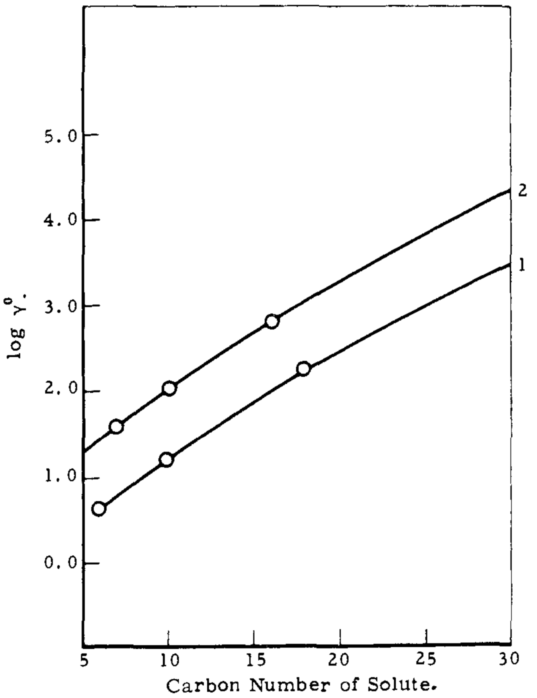

Fig. 4.—Comparison of activity coefficients in triethylene glycol: solvents: 1, *n*-alkylbenzene; 2, *n*-alkanes.

for the first series members (c term important), the two plots are displaced with respect to one another by an amount which may be associated with the differences in the K_p and K_{AB}. Second, except in the first members, the two curves are substantially parallel with slopes which are characterized primarily by the coefficient B_p, but also are affected somewhat by the D term when broad carbon number ranges are considered. These two effects have been observed over very broad ranges of solute types and solvents. They may be expected in virtually all solutions except in those in which a strong chemical interaction occurs between the two solution components.

For the instance in which the solute is held constant and the solvent is varied within an homologous series, the above formulation gives for the activity coefficient of the solute

$$\log \gamma^0 = \left[A + \frac{F}{n' + F'}\right] + \left[\frac{B}{n'}\right] n + \frac{C}{n + C'} + D(n - n')^2 \quad \text{(VI)}$$

where the square brackets enclose terms which were held constant in the discussion just preceding. Examples of the relation of these terms to solvent carbon number are shown for the case of alkanones as solutes in primary alkanols as solvent are shown in Fig. 5. Here the terms have been based on ten systems involving alkanones from propanone to heptanone-3 and alkanols from methanol to 1-octanol. It is clear that K and B_p coefficients of the preceding discussion become smaller as the carbon number of the solvent is increased (over-all polarity decreased by dilution with methylene groups). In terms of the plot in Fig. 4, this results in a decrease in the displacement of the two curves and in a lowering of their slopes and has important bearing on the "type" and molecular weight selectivities of solvents.

Some Relations between Solute Vapor Pressure and Structure.—Useful regularities may also be observed in the P^0's of solute components at constant

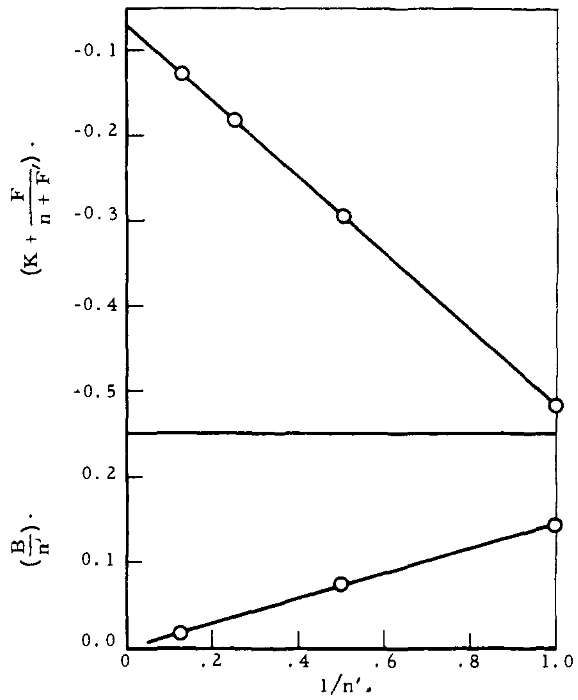

Fig. 5.—Effects of carbon number of solvent; *n*-alkanones in alcohol solvents; *n'* = carbon number of solvent.

temperature as their structure varies, though the structural changes which are important to P^0 are in some cases different from those important to γ^0's. Plots of log P^0 as a function of carbon number are shown in Fig. 6.

TABLE II

CONSTANTS FOR ACTIVITY COEFFICIENT CORRELATIONS

	Alkane and alkylbenzene solutes				
Solvent	Heptane at 90°	2-Butanone at 90°	Phenol at 90°	Triethylene glycol at 90°	Water at 25°
K_p	0	0.33_0	0.62_0	0.68_0	0.69
K_{AB}	0.20_2	0.23_9	$.42_0$	$.73_0$	3.55
B_p	0	0.019	$.058_1$	.134	0.63
C	-0.35_0	-0.35_0	-0.35_0	-0.35_0	(0.46_6)
C'	−4	−4	−4	−4	−4
D	−0.0006	−0.0006	−0.0006	−0.0006	.....

Within homologous series, particularly over the fairly limited ranges of carbon number which are usually of interest in a GLPC separation, the P^0's of successive members of the series differ by a roughly constant factor. This factor, which corresponds to the increment log P^0 (*i.e.*, the free energy of vaporization) per methylene group added to the structure, frequently varies somewhat in the first several members of a given series, but fairly rapidly approaches a constant value for a large number of homologous series. Examples derived from vapor pressure data of the American Petroleum Institute, Project 44, which illustrate this effect are shown in Table III. Here, the contribution to log P^0 per methylene group varies between the extremes of about 0.2 and 0.5. If, however, the first one or two series members are excluded, the contribution to log P^0 is about 0.35 to within about 0.03 in log P^0 or about 7% in P^0 itself, even over the wide range of polarity represented by the examples shown.

Other structural changes also show useful regularities, and in many cases detailed configurational effects become important. Examples illustrating the consistency of contributions for methyl groups and for hydroxyl groups using the same series of compounds as in the above are shown in Tables IV and V. In the case of the methyl group contribution to the log P^0 of paraffins, an average value of about 0.25 holds with about the same precision as in the methylene case. It is of particular interest that moderate branching is much more important to P^0 than to γ^0. In the case of the contribution to the log P^0 of alkanols the average value is somewhat lower and cannot be applied with very good precision, particularly if detailed positional factors are not taken into account. In the case of the contributions of hydroxyl groups to log P^0, an average value of about 1.45 is obtained when the alcohol formed is primary, about 1.08 when secondary and about 0.95 when tertiary. These values are, however, not very precisely maintained, particularly over the first series members for which the data are available.

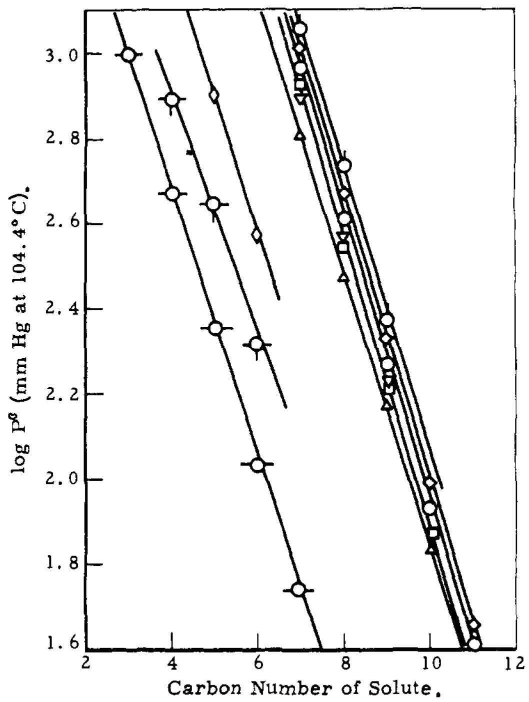

Fig. 6.—Vapor pressures of homologous series members: ○, *n*-alkanes; ȯ, 2-methylalkanes; △, *n*-alkylbenzenes; ▽, *n*-alkylcyclopentanes; ◻, *n*-alkylcyclohexanes; ♢, 1-alkenes; -○-, 1-alkanols; -ọ-, 2-alkanols; ◇, 2-alkanones.

Some Relations between Partition Coefficients and Structure.—In order to illustrate the interplay of solute and solvent properties which can be exploited in GLPC separations the partition coefficients for two "types" of materials, *n*-alkanes and *n*-alkylbenzenes, have been estimated on the above basis for several solvent cases. These cases are those of (1) a hypothetical solvent which forms ideal solutions with all components, (2) a non-polar solvent (C_{30} paraffin) which gives negative deviations from Raoult's law ($\gamma^0 < 1$) with low molecular weight paraffins and (3) a fairly strongly polar solvent (triethylene glycol) which gives moderately

TABLE III

CHANGES IN SOLUTE VAPOR PRESSURE IN HOMOLOGOUS SERIES, 85°

	$\log P_n^0 - \log P_{n+1}^0$									
Carbon number, n	1	2	3	4	5	6	7	8	9	10
n-Alkanes	(a)				0.40	0.389	0.389	0.264	0.366	
2-Methylalkanes				0.46[a]	.39	.381	.374	.346		
3-Methylalkanes						.378[a]	.368	.366		
2,2-Dimethylalkanes					.47[a]	.366	.362	.362		
2,3-Dimethylalkanes						.406[a]	.347	.361		
2,4-Dimethylalkanes							.381[a]	.339		
3,3-Dimethylalkanes						.354[a]	.341	.352		
n-Alkylcyclopentanes					.307[a]	.412	.377	.369	.380	.367
n-Alkylcyclohexanes						.260[a]	.416	.359	.372	.368
n-Alkylbenzenes						.406[a]	.358	.334	.373	.362
1-Alkanols	0.213[a]	0.315	0.364	.328	.363					
2-Alkanols			.294[a]	.336	.348					
3-Alkanols				.275[a]	.299					
2-Methyl-1-alkanols				.373[a]	.305					
3-Methyl-1-alkanols					.366[a]					
2-Methyl-2-alkanols				.325[a]	.288					
3-Methyl-2-alkanols					.356[a]					
2,3-Dimethyl-1-alkanols					.372[a]					

[a] First member of series.

TABLE IV

CHANGES IN SOLUTE VAPOR PRESSURE WITH METHYL GROUP ADDITION, 85°

	$\log P_n^0 - \log P_n^0 + \mathrm{CH_2}$							
Carbon number, n	1	2	3	4	5	6	7	8
Alkanes → 2-methylalkanes				0.34[a]	0.30	0.177	0.263	0.227
Alkanes → 3-methylalkanes						.1301[a]	.281	.266
Alkanes → 4-methylalkanes								.228
2-Methylalkanes → 2,2-dimethylalkanes				.26[a]	.27	.239	.220	.208
2-Methylalkanes → 2,3-dimethylalkanes					.26[a]	.375	.341	.228
2-Methylalkanes → 2,4-dimethylalkanes						.256[a]	.256	.221
1-Alkanols → 2-methyl-1-alkanols			0.188[a]	.194	.175			
1-Alkanols → 3-methyl-1-alkanols				.221[a]	.263			
1-Alkanols → 4-methyl-1-alkanols					.267[a]			
2-Methyl-1-alkanols → 2,3-dimethyl-1-alkanols					.322[a]			
2-Alkanols → 3-methyl-2-alkanols				.209[a]	.230			
2-Alkanols → 4-methyl-2-alkanols					.167[a]			
3-Alkanols → 2-methyl-3-alkanols					.143			
2-Alkanols → 2-methyl-2-alkanols			0.001[a]	.032	− .015			
3-Alkanols → 3-methyl-3-alkanols					.018[a]			
2-Methyl-1-alkanols → 2,2-dimethyl-1-alkanols					.199[a]			

[a] First member of series.

TABLE V

CHANGE IN SOLUTE VAPOR PRESSURE WITH HYDROXYL GROUP ADDITION, 85°

	$\log P_n^0 - \log P_n^0 + \mathrm{OH}$					
Carbon number, n	1	2	3	4	5	6
Alkanes → 1-alkanols	[a]			1.615	1.510	1.468
2-Methylalkanes → 2-methyl-1-alkanols				1.56[a]	1.47	1.384
3-Methylalkanes → 3-methyl-1-alkanols						1.476[a]
2,2-Dimethylalkane → 2,2-dimethyl-1-alkanols						1.532[a]
3,3-Dimethylalkane → 3,3-dimethyl-1-alkanols						(1.432)[a]
Secondary OH						
Alkane → 2-alkanols			[a]	1.29	1.20	0.795
3-Methylalkane → 3-methyl-2-alkanols					(1.17)[a]	1.092
4-Methylalkane → 4-methyl-2-alkanols						(1.066)[a]
3,3-Dimethylalkane → 3,3-dimethyl-2-alkanols						1.040[a]
2-Methylalkane → 2-methyl-3-alkanol						0.982[a]
Tertiary OH						
2-Methylalkanes → 2-methyl-2-alkanols				1.08[a]	0.99	0.884
3-Methylalkanes → 3-methyl-3-alkanols						0.825[a]
2,3-Dimethylalkane → 2,3-dimethylalkanols						0.983[a]

[a] First member of series.

large positive deviations from Raoult's law ($\gamma^0 >> 1$). Log H^0 *versus* carbon number is shown in Fig. 7.

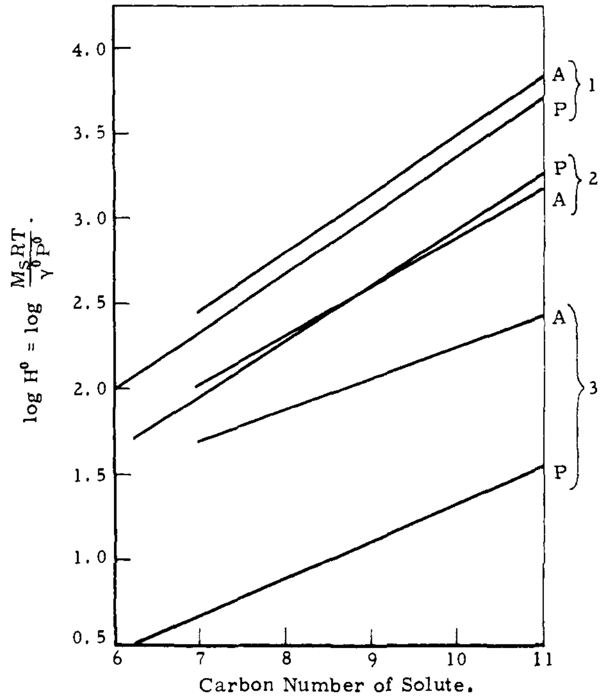

Fig. 7.—Approximate H^0 values for several solvent cases: P, alkanes, A, alkylbenzenes; 1, ideal (M_S = 10) solvent; 2, C_{30} paraffin solvent; 3, triethylene glycol solvent.

In the ideal solvent case, differences in H^0 values arise purely from differences in the vapor pressure of the solutes, and separations with such a solvent might be said to be based purely on solute P^0 or boiling point. It may be noted that alkanes cannot be separated from aromatics with carbon numbers about 0.3 unit higher, that the relative volatilities for alkanes and aromatics of the same carbon number are about 1.25 and that the relative volatilities of successive carbon numbered alkanes or aromatics are about 2.25. The magnitudes of the H^0 values being greater than 100 for all cases shown, all of the component pairs with relative volatilities greater than about 1.1 or so could be reasonably well resolved in a normal column using normal GLPC charge sizes and charging volumes.

In the case of the paraffinic solvent it is apparent that, insofar as the H^0 values of successive carbon numbered hydrocarbon solutes are concerned, P^0 effects predominate and separations are substantially according to boiling point. Insofar as the separations between "types" are concerned, however, the P^0 effects have been substantially overcome by γ^0 value effects with the net result that on the average alkanes and aromatics of the same carbon number can no longer be easily separated. The magnitudes of the H^0 values are lower than in the ideal case. γ^0 value effects tend to increase the magnitudes ($\gamma^0 < 1$) in this case; however, the M_s factor is low ($\sim$1.9) compared to that assumed for the ideal case ($\sim$10) and lowers the magnitudes by a constant factor. The magnitudes are still, however, large enough to give reasonable separation with ordinary columns and sample sizes, provided the relative volatilities are large enough. The absolute magnitudes may, of course, be increased by lowering the temperature somewhat without affecting the relative magnitudes for the various components significantly.

In the case of the polar solvent γ^0 value effects have become quite significant in relation to P^0 effects and result in a considerable change in the basis of separations possible. Insofar as the relative volatilities for successive carbon numbered components of a given type are concerned, the ideal relative volatility has been reduced from roughly 2.25 to about 1.7. Insofar as the relative volatilities of types are concerned the ideal factor of about 1.25 has been increased to about 9. As a result of both the decrease in slope and the relative displacement of the log H^0 curves for the two "types," the carbon number spread between the members of the "types" which cannot be separated has been increased from 0.3 to about 5. The solvent may thus be said to be "type" selective. It may be noted that the general magnitudes of the H^0 values are markedly lower than those of the ideal case. This results almost completely from the large γ^0 values involved, M_s in this case being about 7 as compared to 10 for the ideal case taken. The H^0 values, at least in the cases of the lower numbered hydrocarbons, are rather low and depending on the details of apparatus may be somewhat low for reasonable resolution with ordinary sample sizes and charging volumes. As is generally the case, the magnitudes of the Hv^0 alues may be increased by lowering the temperature. Insofar as γ^0 effects are concerned, this will result in some increase in "type" selectivity and a slight increase in molecular weight selectivity, corresponding to an increase in both "$K_p - K_{AB}$" and in B_p.

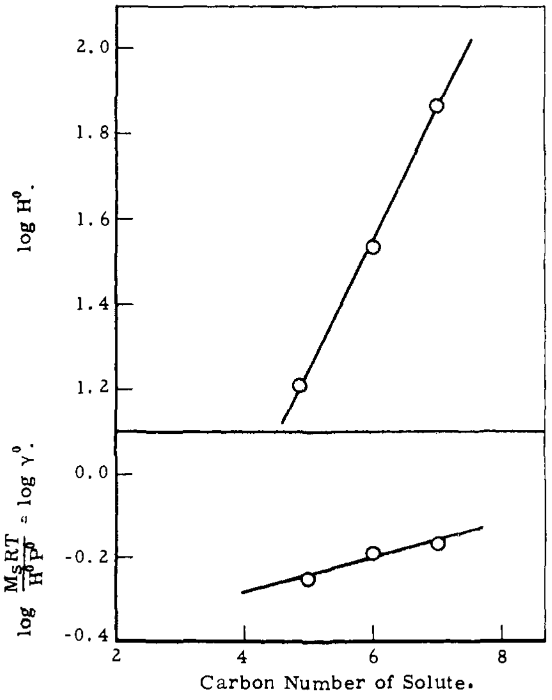

Fig. 8.—Alkanes in squalane solvent.

Plots of log H^0 *versus* carbon number and of log M_sRT/H^0P^0 *versus* carbon number for various homologous series from the three practical GLPC solvents tested in the present work are shown in Fig. 8 through 11 and further illustrate the effects discussed above. In the first case, that of normal alkanes in squalane solvent at 105°, the plots are substantially linear as is to be expected from the γ^0 value and P^0 value relations. The apparent activity coefficients in squalane are somewhat higher than would be expected for the solutes at infinite dilution in a normal paraffin of the same molecular weight (for n-pentane 0.5_6 as compared to an expected value in the region of 0.4_2). This may result in part from the relatively high concentrations encountered in the liquid phase and in part from a consistent error in the amount of solvent in the column used in the determination. It is of interest that the temperature coefficients for these solutes are reasonable in order of magnitude[6] and that the apparent rate change of log γ^0 with carbon number (*ca.* 0.04) is about that expected $(-2D(n-n') = 0.029)$.

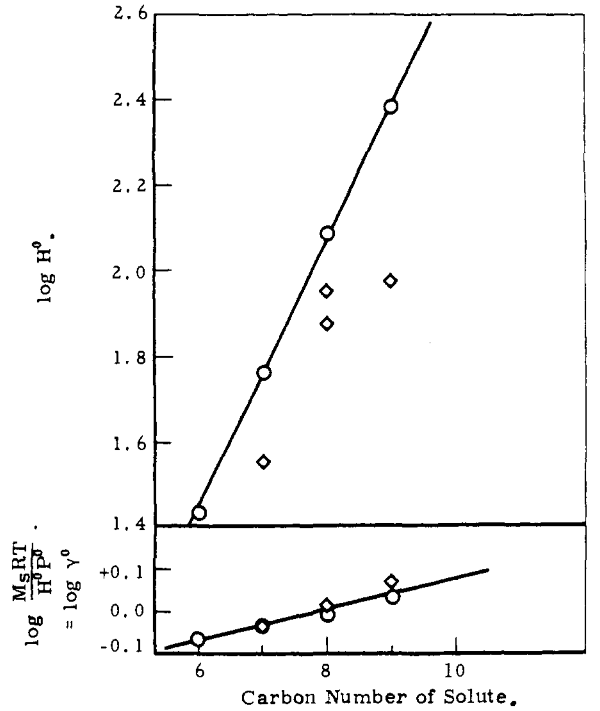

Fig. 9.—Alkanes in diisodecyl phthalate: ○, straight chain: ◇, branched chain.

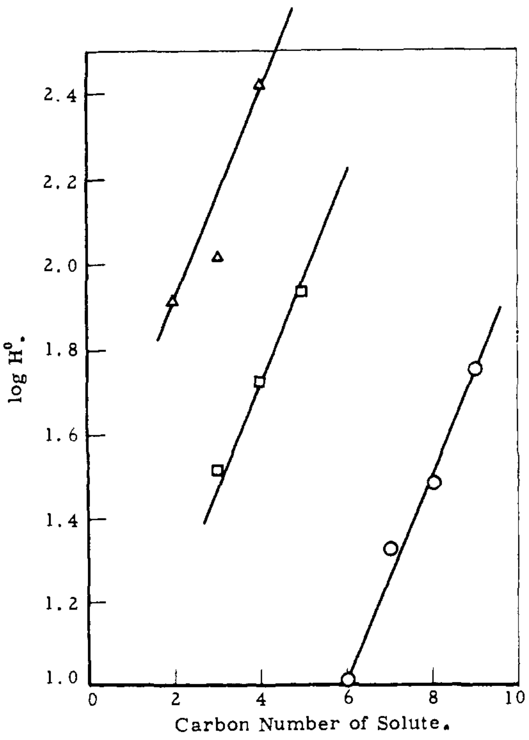

Fig. 10.—n-Alkanes, 1-alkanols and alkanones in Triol solvent: ○, n-alkanes; □, alkanones; △, 1-alkanols.

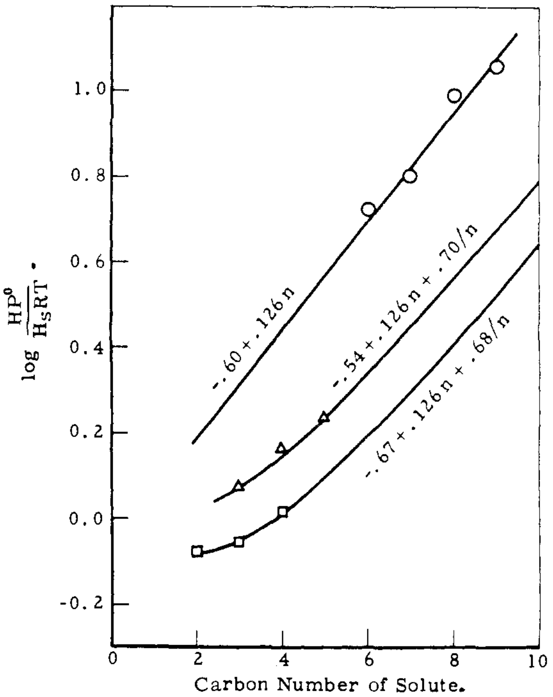

Fig. 11.—n-Alkanes, 1-alkanols and alkanones in Triol solvent: ○, n-alkanes; △, alkanones; □, 1-alkanols.

In the case of diisodecyl phthalate, the n-alkanes show a regular variation of log H^0 with carbon number, but the branched chain alkanes have lower partition coefficients corresponding to their higher P^0's. The log γ^0's, however, are substantially identical with the corresponding carbon numbered normal alkanes as expected from direct solution studies. It is of interest that as a result of the large carbon number of the solvent, the b term would be expected to be small (large n' in Bn/n'). This is apparently the case since the apparent rate change of log M_sRT/H^0P^0 with carbon number is small.

In the case of the Triol solvent, three "types" of substances are shown, n-alkanes, alkanones and alkanols. As is to be expected simply on the basis of differences in polarity and hydrogen bonding, the alkanols form the more ideal solutions, alkanones have moderate positive deviations from Raoult's law, and the normal alkanes have large positive deviations. With this solvent, in contrast to the case with diisodecyl phthalate, "type" differences are sufficiently large to stand out over small inconsistencies of the data, and the apparent activity coefficients have been correlated. Since the range in carbon number is small the *d* terms have been neglected, the B_p determined by the slope of the *n*-paraffin curve, and in the cases of the alkanones and alkanols *c* terms and *a* terms determined from the three data points. In the latter cases the *C*'s are determined as the best slopes of a $\log M_sRT/H^0P^0 - Bn/n'$ *versus* $1/n$ plots and the *K*'s as the intercepts. It is clear that the available data are adequately expressed by the relations derived. It may be noted that "B_p" coefficient for Triol is about the same as for triethylene glycol (see Table II) as might be expected since the "atomic" concentration of the polar hydroxy groups is about the same as in triethylene glycol ($^3/_{12}$ as compared to $^2/_7$).

In addition to the above, several methods of extending GLPC data for homologous series which do not explicitly separate γ^0 and P^0 effects follow directly from the relations discussed above. The first and most broadly applicable of these eliminates P^0 effects and some of the less convenient terms in the γ^0 relations. Consider a given homologous series of solute components in two different solvents, A and B. For such a case, the activity coefficients for the members of any homologous series may be expressed by

$$\begin{aligned} \log \gamma_A^0 &= A_A + B_A(n/n'_A) + C/(n + C') + \\ &\qquad F_A/(n'_A + F'_A) + D(n - n')^2 \\ \log \gamma_B^0 &= A_B + B_B(n/n'_B) + C/(n + C') + \\ &\qquad F_B/(n'_B + F'_B) + D(n - n')^2 \end{aligned} \quad \text{(VII)}$$

It will be recalled that in such expressions the *F* coefficients depend only on the solvent and the *C* coefficients do not depend on the nature of the solvent critically. In addition, the *D* coefficients are small. As a result, the difference in the log γ^0's of the members of an homologous series may be written to a good approximation

$$\log(\gamma_A^0/\gamma_B^0) = K'_A + (B_A/n'_A - B_B/n'_B)n \quad \text{(VIII)}$$

where the difference in the terms involving *F*'s have been included in *K'*, where the terms involving *C*'s cancel out, and the differences in terms involving *D* have been neglected. From VIII and I, the differences in log H^0's in the two solvents may be written

$$\log H_B^0/H_A^0 = \log(M_{sB}/M_{sA}) + K' + (B_A/n'_A - B_B/n'_B)n \quad \text{(IX)}$$

where P^0's have cancelled out exactly. From IX it may be seen that a plot of the differences in log H^0 of the corresponding members of an homologous series for the two solvents may be expected to be linear in the carbon number of the homologous series members. In addition, since IX involves only the solute independent "*B*" coefficients, the slopes of such plots for a given pair of solvents may be expected to be the same for all homologous series. This provides a very good basis on which to estimate partition coefficients when only incomplete data are available.

Plots of this type are shown in Fig. 12 for several alkanes, alkenes, alkanols and alkanones. Here the experimental points scatter somewhat about the four parallel lines drawn in, but the general pattern of behavior is well founded.

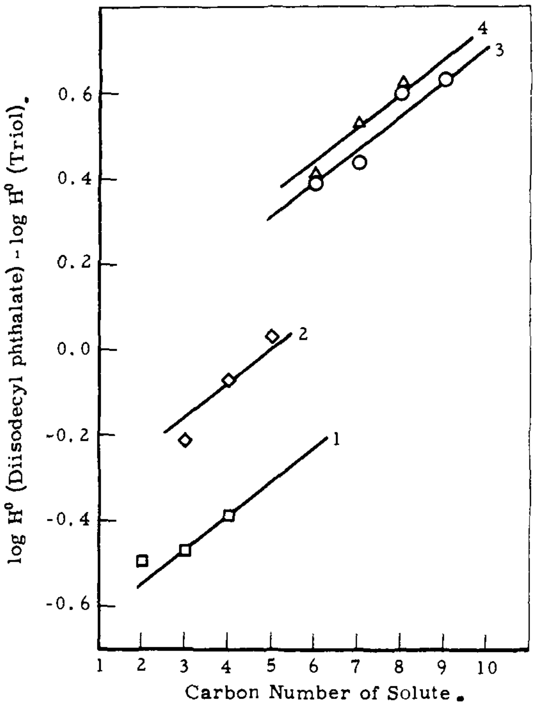

Fig. 12.—Comparison of solvents: 1, 1-alkanols; 2, alkanones; 3, *n*-alkanes; 4, alkenes.

Other methods of extending data may be based on more extensive approximations, and on the basis of experience from direct solution behavior studies cannot be expected to be as broadly applicable as the foregoing case. Frequently the *b* terms of the activity coefficient expression predominate over the other terms in characterizing the change in γ^0 with solute carbon number, particularly if first series members and broad ranges of solute carbon numbers are not considered. In this case for two solvents, A and B, the γ^0's of the members of an homologous series can be expressed

$$\begin{aligned} \log \gamma_A^0 &= K'_A + (B_A/n'_A)n \\ \log \gamma_B^0 &= K'_B + (B_B/n'_B)n \end{aligned} \quad \text{(X)}$$

where the *K*'s include all constant terms. In this case, plots of $\log H^0 - \log P^0$ are expected to be linear in carbon number. This of course, differs from log γ^0 plots discussed above only by the constant $\log M_sRT$.

If first series members are not considered, log P^0 is also frequently linear in carbon number within an homologous series

$$\log P^0 = K + \beta n \quad \text{(XI)}$$

From I, X and XI

$$\begin{aligned} -\log H_A^0 &= K''_A + (\beta + B_A/n'_A)n \\ -\log H_B^0 &= K''_B + (\beta + B_B/n'_B)n \end{aligned} \quad \text{(XII)}$$

This is equivalent to the plots shown by Littlewood, Phillips and Price[14] for their *Vg*. For large parti-

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(14) A. B. Littlewood, C. S. G. Phillips and D. T. Price, *J. Chem. Soc.*, 1480 (1955).

tion coefficients and retention volumes, *i.e.*, log $(V_m + H^0V_s) \simeq$ constant + log (H^0V_s), it is related to the linear plots of log V_R^0 *versus* carbon number shown by Ray.[15] It should be noted, however, that such plots for different homologous series can be expected to be parallel only when the corresponding P^0 curves are also parallel. The slopes for different solvents are in general different.

Eliminating *n* from XII, one obtains

$$\log H_A^0 = -K_A'' + \frac{\beta + B_A/n_A'}{\beta + B_B/n_B'} K_B'' + \frac{\beta + B_A/n_A'}{\beta + B_B/n_B'} \log H_B^0 \quad \text{(XIII)}$$

Here the only term on the right that changes from homologous series member to homologous series member is the one involving H_B^0. Since the coefficient of log H_B^0 is constant within the homologous series, it is clear that a plot of the logarithms of the partition coefficients of the members of an homologous series for one solvent against those of a second solvent is a linear plot. As long as log P^0 plots for different homologous series have the same slope (β), such plots for different homologous series are parallel. Examples of such plots are shown in Fig. 13. In these cases, the curves are parallel.

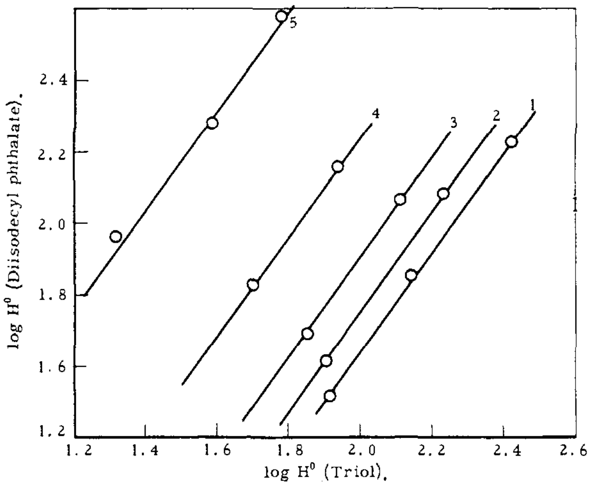

Fig. 13.—Comparison of solvents: 1, 1-alkanols; 2, secondary alkanols; 3, tertiary alkanols; 4, alkanones; 5, *n*-alkanes.

The advantage of this plot over the just preceding one lies primarily in that it gives a graphic illustration of the differences in separation which may be achieved with the two solvents compared. Thus a vertical line intersects the plots at carbon numbers which have the same partition coefficients and indicates the materials that cannot be separated with the solvent represented by the abscissa. A horizontal line gives the corresponding information for the solvent represented on the ordinate.

It will be noted that in equation XIII β is the order of 0.35 (Table III) and B_A/n_A' or B_B/n_B' may take values from 0 to about 0.2 for practical solvents (Table II). The coefficient of log H_B^0 may consequently be expected to fall within the limits of unity and about 1.6. For the special case in which the B/n' coefficients are the same for both solvents, the slopes of the plots are simply unity. In this special case equation XIII may be reduced to

$$V_{RA}^0 = (K_B'' - K_A'')(V_{sA}/V_{sB})(V_{RB}^0 - V_{mB}) + V_{mA} \quad \text{(XIV)}$$

where the V_R^0's are limiting retention volumes for the homologous series members, and the V_s's and V_m's are the volumes of the liquid phase and the gas phase, respectively, in the two columns. It is clear that equation XIV indicates a linear relation between the limiting retention volumes of the homologous series members determined with the two solvents but that the slopes and intercepts for different homologous series are in general different. This is just the linear correlation plot of V_A^0's *vs.* V_B^0's shown by James and Martin.[2]

In addition to the above, it has been useful to correlate partition coefficients of solutes in a given solvent directly with structure very much as reported by Littlewood, Phillips and Price.[14] Incremental values of log H^0 corresponding to various structural changes are systematically determined in order to provide a basis for estimating partition coefficients for solutes which have not been determined. Such a procedure is ultimately based on the premise that plots of log H^0 *versus* carbon number give parallel straight lines for all homologous series. As is clear from the above discussions of γ^0's and P^0's, this can be expected to hold to within 5–10% only for the higher members of homologous series. It is also clear that, although moderate chain branching of hydrocarbon groupings does not strongly affect γ^0's, such structural differences must be taken into account when H^0's are correlated.

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EMERYVILLE, CAL.

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[15] N. H. Ray, *J. Appl. Chem.*, **4**, 21 (1954).