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## COMPARISON OF SOLVENT MODELS FOR CHARACTERIZING STATIONARY PHASE SELECTIVITY IN GAS CHROMATOGRAPHY

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### SUMMARY

Two experimental approaches to the measurement of stationary phase selectivity using the thermodynamic models proposed by Rohrschneider–McReynolds and Golovnya–Poole are tested theoretically and experimentally to establish their reliability. The retention index difference of Rohrschneider–McReynolds is demonstrated to incorrectly determine selectivity since this difference is largely determined by the difference in solubility of the *n*-alkane retention index markers in the polar and non-polar phases. Also, the assumption that the contribution of dispersion to the index value is equivalent to the retention of a hypothetical *n*-alkane on squalane with the same retention time as the test solute on the polar phase fails to take account of the differences in the free energy of solution per index unit on the compared phases. These inconsistencies are not found when differences in the partial molar Gibbs free energy of solution for a series of test solutes are used to determine stationary phase selectivity. A general equation relating the free energy differences to retention index differences is derived and indicates that there is no simple relationship between the two models which, therefore, predict very different selectivity changes for the same test solutes for a group of compared phases. It is concluded that the ordering of stationary phases with respect to their ability to interact selectively with a particular test solute should be determined from free energies of solution (determined from gas–liquid partition coefficients corrected for interfacial adsorption) and that the use of the McReynolds phase constants be abandoned for this purpose.

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### INTRODUCTION

The selectivity of the chromatographic system and thus the ease of obtaining a particular separation in gas–liquid chromatography (GLC) is determined primarily by differences in solute vapor pressures and the strength of solute–solvent interactions in the liquid phase<sup>1,2</sup>. To a first approximation at normal column operating pressures and sample sizes it can be assumed that samples behave ideally in the gas phase with the inert gases commonly used as carriers. A theoretical understanding of selectivity differences between individual solvents is unavailable and must await the development of exact descriptions of the intermolecular forces that exist between complex molecules as are encountered in gas chromatography (GC). A pragmatic solution to this problem

has been found by adopting several largely empirical experimental approaches to characterize the solvent properties of stationary phases used in GC. The most widely used approach is that of Rohrschneider as later modified by McReynolds (see refs. 3–11). In this instance solvent selectivity was quantitatively determined by the differences in the retention index values of a series of test solutes chosen to express particular solute–solvent interactions for the stationary phase to be characterized with respect to the properties (retention index values) for the same solutes measured on squalane as a non-polar reference phase. Rohrschneider–McReynolds phase constants are commonly used by vendors of chromatographic supplies to define the application areas for new phases and by users to identify phases having identical (or similar) properties. In spite of the more or less universal adoption of the Rohrschneider–McReynolds phase constants it has been suggested that these values may be unreliable due to a combination of theoretical and practical deficiencies in the protocol used for their calculation<sup>10–17</sup>. Briefly summarized these problems can be stated to be: (1) a failure to account for the contribution of interfacial adsorption, particularly for the retention index standards, as a significant retention mechanism; (2) the phase constants are composite terms embodying both the contribution of selective solute–solvent interactions and solubility differences of the *n*-alkane retention index markers on the compared phases (the latter contribution tending to dominate); and (3) there is insufficient retention of some test solutes on certain phases to permit the determination of the phase constants with the required degree of accuracy.

An alternative approach to that of Rohrschneider–McReynolds has been adopted by Golovnya–Poole (see refs. 10, 11, 13, 16 and 18). These workers defined differences in stationary phase selectivity as equivalent to the differences in the partial molar Gibbs free energy of solution for a series of test solutes on the phases to be characterized and on a reference phase exhibiting minimal selectivity. In most cases the same test solutes as used by McReynolds have been used in these studies as well as the adoption of squalane as the reference phase exhibiting minimal selectivity. In general there are substantial differences between the ranking of individual phases by their ability to interact with a particular test solute using phase constants derived by the two different approaches. The purpose of this paper is to demonstrate why this difference arises based on fundamental and experimental considerations, to show how the two selectivity scales can be interrelated, and to provide a corrected set of experimental data to be used to test new hypotheses that may be developed in the future.

## EXPERIMENTAL

General experimental conditions and sources of phases and standards, etc. are identical with those reported elsewhere<sup>12,13</sup>. Common abbreviations and trade names for stationary phases are identified in Table I. All GC measurements were made by headspace injection of test solutes under infinite dilution conditions conforming to the linear portion of the sorption isotherms. All peak shapes were symmetrical and there was no dependence of retention on sample size in the measurement region. On-column silanization of packings prepared from non-polar phases was used as required to control peak tailing<sup>13</sup>. The column temperature was 80.8°C ( $\pm 0.2^\circ\text{C}$ ) and the column pressure drop less than 1 atm (determined to  $\pm 1$  mmHg) in all cases. Nitrogen was used as carrier gas. Retention volumes are uncorrected for gas phase non-ideality since

TABLE I

GAS-LIQUID PARTITION COEFFICIENTS FOR McREYNOLDS TEST SOLUTES ON SOME REPRESENTATIVE STATIONARY PHASES AT 80.8°C

The uncertainty in the measurements is given by the standard deviation in parenthesis. X' = benzene, Y' = butanol, Z' = 2-pentanone, U' = nitropropane, S' = pyridine, H' = 2-methyl-2-pentanol, J' = iodobutane, K' = 2-octyne, L' = dioxane and M' = *cis*-hydrindane.

Stationary phase <sup>a</sup>	Gas-liquid partition coefficient									
	X'	Y'	Z'	U'	S'	H'	J'	K'	L'	M'
Squalane	80.8 (0.5)	47.8 (1.2)	67.2 (0.8)	80.9 (1.0)	114.7 (2.2)	111.9 (1.1)	310.8 (2.9)	420.1 (4.4)	81.4 (0.7)	1394.1 (15.0)
OV-17	77.6 (1.0)	69.6 (1.0)	94.8 (0.8)	198.4 (10.6)	196.9 (1.2)	104.9 (2.5)	258.2 (3.7)	312.4 (5.3)	129.2 (3.2)	688.8 (14.1)
OV-105	61.5 (3.0)	87.0 (8.2)	78.9 (2.5)	126.3 (3.1)	118.9 (3.5)	110.1 (3.7)	186.2 (5.2)	256.9 (7.4)	84.7 (2.3)	575.0 (14.5)
OV-330	88.9 (0.7)	199.5 (3.7)	111.9 (0.9)	350.4 (2.6)	291.2 (3.0)	197.2 (1.3)	247.3 (4.9)	247.2 (4.7)	161.0 (5.7)	432.9 (2.9)
OV-225	69.1 (0.1)	133.7 (2.4)	129.6 (1.4)	378.6 (3.8)	256.7 (4.5)	152.2 (1.2)	197.4 (1.6)	167.2 (2.7)	148.1 (9.6)	320.4 (3.9)
QF-1	45.6 (1.1)	53.4 (4.2)	136.8 (4.0)	274.1 (7.9)	146.9 (5.0)	85.9 (3.2)	118.4 (4.0)	100.2 (3.5)	102.2 (1.7)	228.0 (7.0)
Carbowax 20M	97.6 (0.4)	292.1 (4.8)	114.2 (0.5)	483.6 (1.9)	401.2 (4.6)	212.9 (1.5)	204.3 (2.0)	180.3 (3.9)	199.6 (0.7)	264.1 (3.3)
DPAT	80.2 (12.9)	583.3 (14.1)	177.0 (5.3)	479.2 (12.0)	—	425.0 (11.1)	143.4 (2.9)	74.8 (2.5)	229.8 (6.0)	130.8 (1.7)
DEGS	59.4 (2.7)	240.2 (6.2)	97.9 (1.8)	372.8 (12.2)	—	186.9 (4.8)	89.9 (3.6)	68.7 (2.7)	236.1 (4.5)	86.1 (2.3)
BAT	37.6 (0.8)	658.4 (25.0)	203.6 (9.5)	304.7 (12.6)	—	476.7 (17.9)	74.2 (2.5)	38.2 (1.0)	406.3 (9.6)	79.0 (4.1)
sBAT	38.3 (2.7)	795.8 (15.0)	249.1 (3.1)	355.8 (9.0)	—	553.9 (11.2)	74.4 (2.3)	38.7 (2.8)	505.2 (11.7)	65.2 (3.6)
TCEP	63.4 (2.4)	205.0 (1.3)	133.7 (2.4)	543.1 (3.4)	424.9 (3.0)	139.7 (1.0)	92.3 (2.3)	62.6 (2.4)	245.9 (3.3)	68.1 (0.5)
OV-275	40.9 (1.2)	110.6 (4.4)	67.7 (3.0)	313.1 (13.1)	225.5 (7.8)	65.2 (3.1)	49.6 (2.4)	25.5 (1.2)	126.4 (4.7)	37.6 (3.1)

<sup>a</sup> Squalane = 2,6,10,15,19,23-hexamethyltetracosane, OV-17 = poly(phenylmethylsiloxane), OV-105 = poly(cyanopropylmethylphenylmethylsiloxane), OV-330 = dimethylsilicone/Carbowax copolymer, QF-1 = poly(trifluoropropylmethylsiloxane), Carbowax 20M = poly(ethylene glycol), DPAT = di-*n*-propylammonium thiocyanate, DEGS = poly(diethyleneglycol succinate), BAT = *n*-butylammonium thiocyanate, sBAT = *sec*-butylammonium thiocyanate, TCEP = 1,2,3-tris(2-cyanoethoxypropane) and OV-275 = poly(dicyanoallylsiloxane).

these corrections were found to be small for the experimental conditions employed using the few accurately determined virial coefficients available<sup>19</sup>.

Gas-liquid partition coefficients were calculated by linear extrapolation of plots of  $V_N^*/V_L$  vs.  $1/V_L$  based on eqn. 1:

$$\frac{V_N^*}{V_L} = K_L + (A_{GL}K_{GL} + A_{LS}K_{GLS}) \frac{1}{V_L} \quad (1)$$

where  $V_N^*$  is the net retention volume per gram of packing;  $V_L$  the volume of liquid phase per gram of packing;  $K_L$  the gas-liquid partition coefficient;  $A_{GL}$  the gas-liquid interfacial area;  $K_{GL}$  the coefficient for adsorption at the gas-liquid interface;  $A_{LS}$  the gas-liquid interfacial area; and  $K_{GLS}$  the coefficient for adsorption at the support surface.

Values for the gas-liquid partition coefficients of test solutes are given in Table I together with the uncertainty in their determination. These values supercede those given in ref. 13 which have been corrected for an error in the extrapolation procedure which affected the accuracy of some  $K_L$  values. The partition coefficients for the *n*-alkane and 2-alkanone retention index markers were fitted to eqn. 2:

$$\log K_L = A + Bn \quad (2)$$

where  $B$  is the slope of the plot of  $\log K_L$  vs. carbon number  $n$  and  $A$  is a constant for any particular phase.  $A$  gives the intercept for  $n = 0$  on the same plot and  $n$  the number of carbon atoms for the *n*-alkanes and the number of carbon atoms minus 2 for the 2-alkanones. The coefficients obtained by linear regression are summarized in Table II.

The retention index for each test solute was determined from the adjusted retention time using the standard procedure<sup>1</sup>. Retention index values corrected for interfacial adsorption were calculated using eqn. 3:

$$I_p^c(X) = 100Z + 100 \frac{\log K_L^X - \log K_L^Z}{\log K_L^{Z+1} - \log K_L^Z} \quad (3)$$

where  $I_p^c(X)$  is the retention index for solute X corrected for interfacial adsorption on

TABLE II

COEFFICIENTS FOR CALCULATING PARTITION COEFFICIENTS FOR *n*-ALKANES AND 2-ALKANONES (EQN. 2)

Stationary phase	<i>n</i> -Alkanes		Correlation coefficient ( $r^2$ )	2-Alkanones		Correlation coefficient ( $r^2$ )	$\Delta G_k^0(\text{CH}_2)^p$	
	<i>B</i>	<i>A</i>		<i>B</i>	<i>A</i>		<i>n</i> -Alkanes	2-Alkanones (cal/mol)
Squalane	0.361	-0.4180	1.000	0.358	0.7673	1.000	-585	-579
OV-17	0.325	-0.5596	0.999	0.317	1.0517	0.999	-525	-513
OV-105	0.314	-0.3339	1.000	0.311	0.9841	0.999	-508	-503
OV-330	0.302	-0.6023	1.000	0.298	1.1844	0.999	-488	-482
OV-225	0.293	-0.6556	1.000	0.284	1.2894	0.999	-469	-459
QF-1	0.262	-0.3152	1.000	0.270	1.3499	0.999	-424	-437
Carbowax 20M	0.264	-0.5754	0.999	0.265	1.2939	0.999	-427	-428
DPAT	0.228	-0.6058	1.000	0.239	1.5658	0.999	-369	-386
DEGS	-	-	-	0.218	1.3653	0.999	-	-352
BAT	0.223	-0.8211	0.999	0.215	1.6994	0.997	-361	-347
sBAT	0.188	-0.5733	0.998	0.204	1.8350	0.998	-304	-330
TCEP	-	-	-	0.199	1.5552	0.999	-	-322
OV-275	-	-	-	0.180	1.3233	0.998	-	-330

phase P;  $K_L^X$  the gas-liquid partition coefficient for solute X;  $K_L^Z$  the gas-liquid partition coefficient for an  $n$ -alkane with  $Z$  carbon atoms eluting immediately before solute X; and  $K_L^{Z+1}$  the gas-liquid partition coefficient for an  $n$ -alkane with  $Z + 1$  carbon atoms eluting after solute X.

When the 2-alkanones were used as the fixed points on the retention index scale, eqn. 3 was used with  $Z$  equal to the number of carbon atoms minus 2. Phase constants according to McReynolds were calculated from retention index differences using eqn. 4:

$$\text{Phase constant} = \Delta I^X = I_P^X - I_{SQ}^X \quad (4)$$

where  $I_P^X$  is the retention index for test solute X on stationary phase P; and  $I_{SQ}^X$  the retention index for test solute X on squalane.

Phase constants corrected for interfacial adsorption or based on the 2-alkanone retention index scale were calculated by substituting the appropriate values of the retention index into eqn. 4.

The partial molar Gibbs free energy of solution,  $\Delta G_K^0$ , for the test solutes was calculated from the gas-liquid partition coefficient,  $K_L^X$ , according to eqn. 5:

$$(\Delta G_K^0 X)^P = -2.3RT_C \log K_L^X \quad (5)$$

where  $(\Delta G_K^0 X)^P$  is the partial molar Gibbs free energy of solution of solute X on phase P;  $R$  the universal gas constant ( $1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$ ); and  $T_C$  the column temperature (K).

The difference in free energies for solute X on two compared phases is given by eqn. 6

$$\partial(\Delta G_K^0 X)_{SQ}^P = (\Delta G_K^0 X)^P - (G_K^0 X)^{SQ} \quad (6)$$

where  $\partial(\Delta G_K^0 X)_{SQ}^P$  is the difference in partial molar Gibbs free energy of solution for solute X on stationary phase P and squalane. The partial molar Gibbs free energy of solution for a methylene group,  $\Delta G_K^0(\text{CH}_2)^P$  was calculated according to eqn. 7:

$$\Delta G_K^0(\text{CH}_2)^P = -2.3RT_C B_P \quad (7)$$

where  $\Delta G_K^0(\text{CH}_2)^P$  is the partial molar Gibbs free energy of solution for a methylene group on phase P; and  $B_P$  the slope of  $\log K_L$  vs. carbon number for the  $n$ -alkane or 2-alkanones on phase P. Values for the variable  $B_P$  together with  $\Delta G_K^0(\text{CH}_2)^P$  are given in Table II.

## RESULTS AND DISCUSSION

A good starting point is the thermodynamic definition of the phase constant as proposed by Rohrschneider<sup>3,4</sup>. With respect to Fig. 1, which shows a plot of  $\log K_L$  against carbon number for a homologous series of  $n$ -alkanes on squalane and Carbowax 20M, used to determine the phase constant for solute X (experimental data for dioxane are used in the figure shown). The retention index value for solute X, by definition, is equal to 100 times the carbon number of the hypothetical  $n$ -alkane that

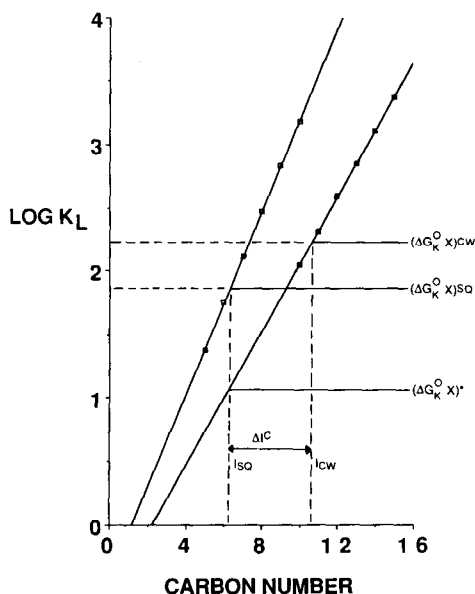


Fig. 1. Plot of the logarithm of the gas-liquid partition coefficients for  $n$ -alkanes as a function of carbon number on Carbowax 20M ( $\circ$ ) and squalane ( $\square$ ). The test solute, X, was dioxane. The free energy scale is plotted on the right without units and is related to  $K_L$  through eqn. 5.

co-elutes with solute X on both phases and the stationary phase selectivity constant to the difference in retention index values as defined by eqn. 4. In thermodynamic terms Rohrschneider identified the difference in retention index values,  $\Delta I$ , with the difference in the partial molar Gibbs free energy of solution for solute X on the polar phase and squalane as a non-polar reference phase according to eqn. 8:

$$\Delta I^R = 100 \frac{(\Delta G_K^0 X)^P - (\Delta G_K^0 X)^*}{\Delta G_K^0 (\text{CH}_2)^P} \quad (8)$$

where  $\Delta I^R$  is the calculated value of  $\Delta I^C$  according to Rohrschneider and  $(\Delta G_K^0 X)^*$  is the partial molar Gibbs free energy of solution for a hypothetical  $n$ -alkane co-eluting with solute X on squalane and having the same carbon number as the  $n$ -alkane used to calculate  $(\Delta G_K^0 X)^*$  on the polar phase using eqns. 2 and 5. The correctness of eqn. 8 is easily tested by inserting experimental values into eqn. 8 and comparing the calculated phase constants with those determined experimentally, Table III. As can be seen there is excellent agreement between the calculated,  $\Delta I^R$ , and experimental values of  $\Delta I$  corrected for contributions to retention arising from interfacial adsorption,  $\Delta I^C$ . Uncorrected values of  $\Delta I$ , calculated directly from adjusted retention times as is normally done, show substantial variation from the calculated values for the polar phases. For the most polar phases investigated, DEGS, TCEP and OV-275 the  $n$ -alkane retention index markers are retained predominantly by interfacial adsorption and appropriate values for  $\Delta I^C$  cannot be calculated. This problem is generally associated with the properties of the  $n$ -alkanes as can be seen by contrasting the plots of Figs. 2 and 3 which represent data for  $n$ -decane and 1-nitropropane on a number of

TABLE III

CALCULATION OF McREYNOLDS PHASE CONSTANTS AT 80.83C ACCORDING TO THE PROCEDURE OF ROHRSCHEIDER

Stationary phase	Index difference	Test solute				
		Benzene	Butanol	2-Pentanone	Nitropropane	Dioxane
OV-17	$\Delta I$	111	156	160	239	179
	$\Delta I^C$	110	158	158	235	177
	$\Delta I^R$	110	158	158	236	177
OV-105	$\Delta I$	34	145	91	134	77
	$\Delta I^C$	32	143	89	132	75
	$\Delta I^R$	32	143	89	132	75
OV-330	$\Delta I$	206	381	261	404	290
	$\Delta I^C$	201	380	256	398	285
	$\Delta I^R$	201	380	256	399	285
OV-225	$\Delta I$	213	370	326	469	325
	$\Delta I^C$	207	368	323	460	320
	$\Delta I^R$	210	372	326	465	323
Carbowax 20M	$\Delta I$	308	541	357	559	420
	$\Delta I^C$	327	571	375	591	444
	$\Delta I^R$	327	571	375	591	444
QF-1	$\Delta I$	116	203	320	413	250
	$\Delta I^C$	109	195	314	407	241
	$\Delta I^R$	109	195	314	407	241
DPAT	$\Delta I$	430	859	606	761	632
	$\Delta I^C$	457	898	630	797	656
	$\Delta I^R$	457	897	629	797	656
BAT	$\Delta I$	404	1019	751	808	856
	$\Delta I^C$	430	1051	781	838	893
	$\Delta I^R$	430	1050	781	838	892

phases of different polarity. 1-Nitropropane, which can be considered representative of the properties of the first five McReynolds test solutes, is retained by gas-liquid partitioning on all phases while *n*-decane is retained by a mixed retention mechanism on many phases. The model proposed by Rohrschneider, expressed by eqn. 8, is fundamentally sound for predicting values of  $\Delta I$  when retention of the *n*-alkanes and test solutes occurs solely by gas-liquid partitioning. It is not applicable to those situations where either the test solute, or more likely, the *n*-alkane retention index standards are retained predominantly by interfacial adsorption. Experimental values of  $\Delta I$  on polar phases are unreliable with respect to the thermodynamic model of eqn. 8.

Eqn. 8 can be derived directly from the equations for a straight line from Fig. 1 and consequently any homologous series of retention index standards that obeys eqn. 2 could be substituted for the *n*-alkanes. Using the 2-alkanones, which are retained largely by partitioning on non-polar and polar phases, the limitation that eqn. 8 can be applied only to non-polar and moderately polar phases using the *n*-alkane retention index standards is removed, Table IV. There is excellent agreement between the values of  $\Delta I^C$  and  $\Delta I^R$  for all phases but on the other hand, if the phases are ranked in order of their  $\Delta I^C$  values for their ability to interact with a given test solute there is

only poor agreement in order between the phases ranked on the scale determined with the 2-alkanone and *n*-alkane retention index standards. Whereas it might be reasonable to assume that a hypothetical *n*-alkane experiences the same magnitude of interactions in squalane and on the polar phase (as is implied in the derivation of eqn. 8) this would seem to be unrealistic for the 2-alkanones which have modest dipole moments (*ca.* 2–3 D) and a reasonable potential for significant induction, orientation, and solvent proton–donor interactions in the compared phases. In terms of eqn. 8 this difference is reflected in the different values of  $(\Delta G_R^\circ X)^*$  since the values of  $(\Delta G_R^\circ X)^P$  and  $\Delta G_R^\circ(\text{CH}_2)^P$  are not affected by the choice of homologous retention index standards provided that eqn. 2 is obeyed. The 2-alkanones are more sensible retention index standards than the *n*-alkanes for the accurate prediction of retention but should not be used for the specific application of determining selectivity phase constants.

Golovnya–Poole have equated the quantitative differences in stationary phase selectivity with the difference in the partial molar Gibbs free energy of solution of the test solute on a polar phase and on a reference phase exhibiting minimum selectivity as described by eqn. 6. As can be seen from Fig. 1 this approach differs significantly in the manner that the non-polar contribution to retention is estimated (it is reasonable to assume that the non-polar retention contribution includes contributions from induction as well as dispersion for the retention of polar test solutes). It has the further practical advantage that this approach is not limited by the problems associated with the use of the retention index system discussed above.

Golovnya and co-workers<sup>16,18,20,21</sup> have derived several relationships between the retention index of a solute and solution thermodynamic parameters that can be used as the basis to derive a general equation relating Rohrschneider's  $\Delta I$  parameter to

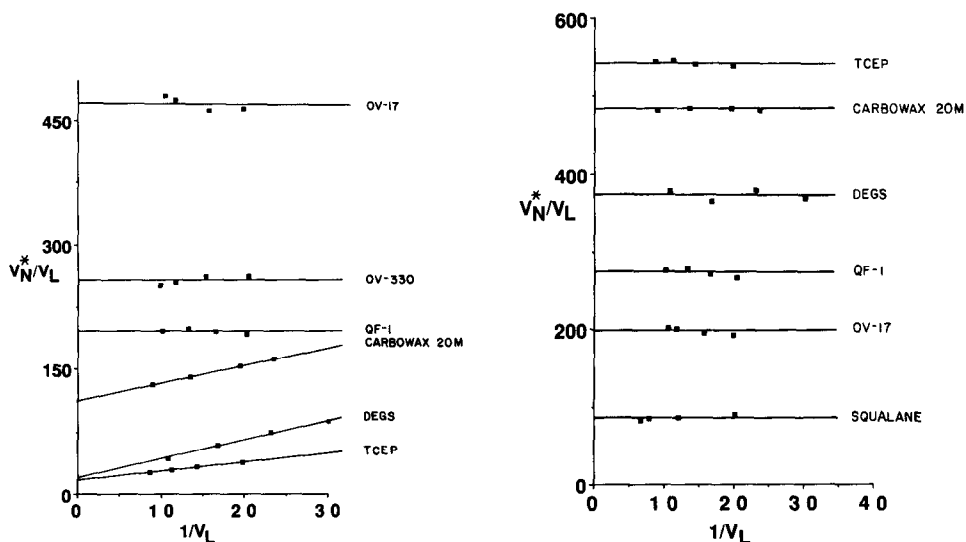


Fig. 2. Plot of  $V_N^*/V_L$  vs.  $1/V_L$  for *n*-decane on a series of stationary phases of different polarity. The stationary phases are identified in Table I.

Fig. 3. Plot of  $V_N^*/V_L$  vs.  $1/V_L$  for 1-nitropropane on a series of stationary phases of different polarity. The stationary phases are identified in Table I.



TABLE IV

CALCULATION OF McREYNOLDS PHASE CONSTANTS AT 80.8°C USING 2-ALKANONES AS RETENTION INDEX STANDARDS

Stationary phase	Index difference	Test solute			
		Benzene	Butanol	Nitropropane	Dioxane
OV-17	$\Delta I$	-53	-8	76	19
	$\Delta I^C$	-54	-5	75	15
	$\Delta I^R$	-54	-5	75	15
OV-105	$\Delta I$	-56	57	41	-14
	$\Delta I^C$	-60	52	41	-16
	$\Delta I^R$	-60	52	41	-15
OV-330	$\Delta I$	-60	121	139	28
	$\Delta I^C$	-62	120	138	24
	$\Delta I^R$	-62	120	138	24
OV-225	$\Delta I$	-128	46	138	-2
	$\Delta I^C$	-125	40	136	-9
	$\Delta I^R$	-125	40	136	-9
Carbowax 20M	$\Delta I$	-56	187	204	63
	$\Delta I^C$	-56	188	207	60
	$\Delta I^R$	-56	188	207	60
QF-1	$\Delta I$	-206	-117	84	-73
	$\Delta I^C$	-204	-118	85	-76
	$\Delta I^R$	-204	-118	85	-76
DPAT	$\Delta I$	-191	243	143	21
	$\Delta I^C$	-177	247	148	14
	$\Delta I^R$	-177	247	149	14
DEGS	$\Delta I$	-142	202	222	135
	$\Delta I^C$	-131	211	-31	143
	$\Delta I^R$	-131	211	-31	143
TCEP	$\Delta I$	-194	124	262	99
	$\Delta I^C$	-194	125	-31	101
	$\Delta I^R$	-194	125	-31	101
OV-275	$\Delta I$	-175	135	277	84
	$\Delta I^C$	-158	146	-36	113
	$\Delta I^R$	-159	146	-36	114

$\partial(\Delta G_k^o X)_{SQ}^P$  defined by eqn. 6. The retention index of a solute can be defined in terms of the gas-liquid partition coefficient of solute X and the retention index standards by eqn. 3. Substituting eqn. 2 into eqn. 3 and rearranging gives eqn. 9:

$$I^X = 100n + \frac{100}{B} (\log K_L^X - A - Bn) \quad (9)$$

which after simplification gives

$$\log K_L^X = \frac{I^X B}{100} + A \quad (10)$$

where  $A$  and  $B$  are the coefficients obtained by linear regression for the retention index standards defined by eqn. 2. The partial molar Gibbs free energy of solution for solute  $X$  is defined by eqn. 5, which after substituting for  $K_L^X$  from eqn. 10, gives

$$(\Delta G_K^{\circ} X)^P = -2.3RT \frac{I_P^X B_P}{100} + A_P \quad (11)$$

and by similar reasoning for squalane

$$(\Delta G_K^{\circ} X)^{SQ} = -2.3RT \frac{I_{SQ}^X B_{SQ}}{100} + A_{SQ} \quad (12)$$

Substituting eqns. 11 and 12 into eqn. 6 and rearranging gives

$$\partial(\Delta G_K^{\circ} X)_{SQ}^P = \frac{2.3RT}{100} (I_{SQ}^X B_{SQ} - I_P^X B_P) + 2.3RT(A_{SQ} - A_P) \quad (13)$$

Substituting for  $I_P^X$  from eqn. 4 into eqn. 13 gives

$$\partial(\Delta G_K^{\circ} X)_{SQ}^P = \frac{2.3RT}{100} [I_{SQ}^X (B_{SQ} - B_P) - \Delta I^X B_P] + 2.3RT(A_{SQ} - A_P) \quad (14)$$

The correctness of eqns. 13 or 14 can be tested using the values of  $I$ ,  $\Delta I$ ,  $A$  and  $B$  given in Tables II–IV to calculate  $\partial(\Delta G_K^{\circ} X)_{SQ}^P$  which can be compared to the experimental values of  $\partial(\Delta G_K^{\circ} X)_{SQ}^P$ . Table V, obtained from the gas–liquid partition coefficients. The

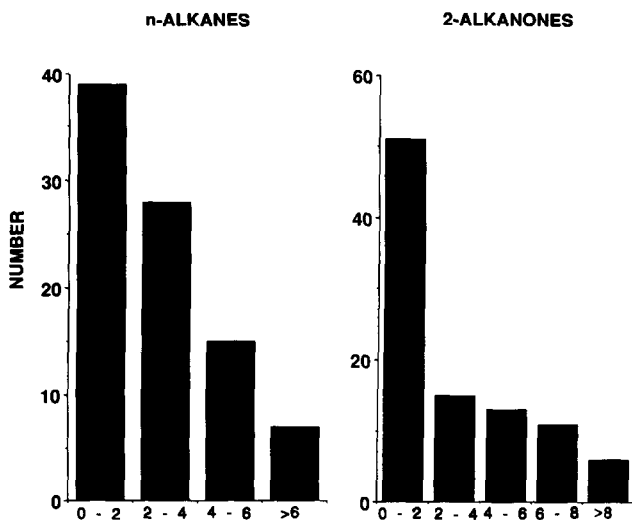


Fig. 4. Frequency distribution of the relative error in  $\partial(\Delta G_K^{\circ} X)_{SQ}^P$  determined by eqn. 13 using  $n$ -alkanes and 2-alkanones as retention index standards and the experimental value determined from  $K_L^X$  for the McReynolds test solutes.

agreement is very good as can be seen from the error frequency distribution in Fig. 4. For the *n*-alkane retention index standards of 89 measurements only seven show a relative error greater than 6% and most of these are associated with benzene and other poorly retained solutes that have a greater uncertainty associated with their determination (Table I). Eqns. 13 and 14 are correct for any homologous series that obeys eqn. 2 and substituting the appropriate values for the 2-alkanones gives a similar goodness of fit to the *n*-alkanes.

Eqn. 14 reveals that there is no simple dependence of  $\partial(\Delta G_{\text{KX}}^{\circ})_{\text{SQ}}^{\text{P}}$  on  $\Delta I^{\text{X}}$  and the magnitude of  $\partial(\Delta G_{\text{KX}}^{\circ})_{\text{SQ}}^{\text{P}}$  changes with the phase specific properties represented by the coefficients *A* and *B* as well as  $\Delta I^{\text{X}}$ . Thus, one can expect no general correlation in the ranking of stationary phases to interact with a particular test solute and the two selectivity scales should be considered as independent and different from each other.

In earlier studies a strong correlation between  $\Delta I^{\text{C}}$  for the McReynolds test solutes and the partial molar Gibbs free energy of solution for a methylene group on a wide range of conventional and liquid organic salt phases has been reported<sup>10,14,15,17,22</sup>. The selectivity index values for  $\Delta I^{\text{C}}$  and  $\partial(\Delta G_{\text{KX}}^{\circ})_{\text{SQ}}^{\text{P}}$  for nitropropane are plotted against *B<sub>P</sub>* in Fig. 5 (*B<sub>P</sub>* is a measure of the solubility of the *n*-alkanes in the polar stationary phase, see eqn. 7). The value of the retention index difference corrected for interfacial adsorption is seen to vary linearly with *B<sub>P</sub>* (except for OV-105 and QF-1) indicating that  $\Delta I^{\text{C}}$  is determined largely by the interactions of the *n*-alkanes with the stationary phase and to a lesser extent by selective interactions of the test solute with the phase. This is probably the reason why the magnitude of the McReynolds phase constants tend to increase monotonously with increasing phase polarity for all test solutes. The  $\partial(\Delta G_{\text{KX}}^{\circ})_{\text{SQ}}^{\text{P}}$  scale shows no similar correlation with *B<sub>P</sub>* which is in agreement with chemical intuition.

TABLE V

THERMODYNAMICALLY CALCULATED PHASE CONSTANTS DERIVED FROM THE PARTIAL MOLAR GIBBS FREE ENERGY OF SOLUTION AT 80.8°C

Test solutes are identified in Table I.  $\partial(\Delta G_{\text{KX}}^{\circ})_{\text{SQ}}^{\text{P}} = (\Delta G_{\text{KX}}^{\circ})_{\text{P}} - (\Delta G_{\text{KX}}^{\circ})_{\text{SQ}}$ . Absolute values for squalane (kcal/mol); X' = -3.085; Y' = -2.717; Z' = -2.956; U' = -3.084; S' = -3.332; H' = -3.315; J' = -4.032; K' = -4.244; L' = -3.091; M' = -5.087.

Stationary phase	$\partial(\Delta G_{\text{KX}}^{\circ})_{\text{SQ}}^{\text{P}}$ (cal/mol)									
	X2'	Y2'	Z2'	U2'	S2'	H2'	J2'	K2'	L2'	M2'
OV-17	28	&264	&242	-633	-380	45	130	208	-325	516
OV-105	191	-421	-113	-316	-25	11	360	346	-28	622
OV-330	-67	-1004	-358	-1033	-655	-398	161	378	-479	821
OV-225	110	-723	-461	-1087	-566	-216	319	647	-421	1033
Carbowax 20M	-133	-1272	-373	-1259	-880	-452	295	594	-630	1169
QF-1	402	-65	-499	-860	-173	191	678	1007	-156	1272
DPAT	5	-1758	-683	-1252	-	-938	543	1212	-729	1663
DEGS	216	-1134	-264	-1076	-	-360	871	1272	-748	1956
BAT	537	-1843	-779	-934	-	-1018	1006	1684	-1129	2017
sBAT	524	-1976	-921	-1043	-	-1124	1004	1675	-1283	2152
TCEP	170	-1023	-483	-1340	-920	-156	853	1338	-777	2121
OV-275	478	-589	-50	-953	-475	380	1289	1969	-309	2539

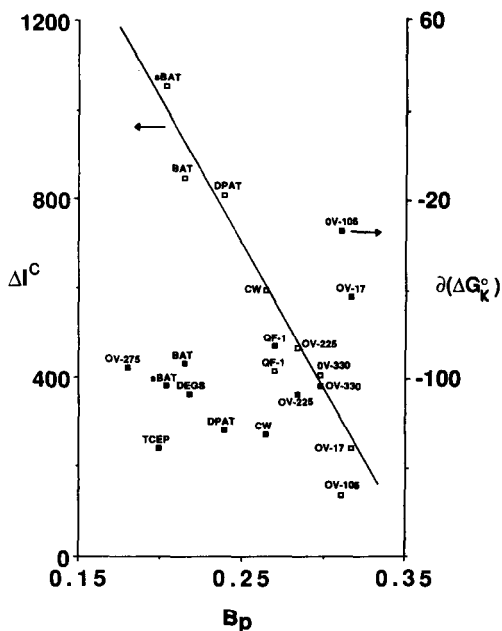


Fig. 5. Plot of  $\partial(\Delta G_k^o X)_{SQ}^P$  (%) and  $\Delta I^C$  ( $\square$ ) against the slope of the plot of eqn. 2 for nitropropane. There is a linear correlation for  $\Delta I^C$  and no correlation for  $\partial(\Delta G_k^o X)_{SQ}^P$ .

The data presented in this paper supports the view that the Rohrschneider-McReynolds system for phase constants should be abandoned as it suffers from experimental and theoretical deficiencies. Mixed retention mechanisms make data for polar phases spurious. The phase constants are determined largely by the character of the retention index standards than by specific interactions with the test solute. Since the Gibbs free energy per index unit varies from one phase to another (typically from 1 to 6 cal/mol) it cannot be assumed that a hypothetical hydrocarbon co-eluting with the test solute on squalane should have the same free energy on a polar phase. These inconsistencies are absent from the  $\partial(\Delta G_k^o X)_{SQ}^P$  scale which is to be preferred on theoretical and practical grounds. A much larger data set for 35 common stationary phases is in preparation to make the  $\partial(\Delta G_k^o X)_{SQ}^P$  scale more useful and to permit studies of the correlation of this parameter with the phase structure.

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