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GAS–LIQUID CHROMATOGRAPHIC STUDY OF THE THERMODYNAMICS OF 1-IODOACETYLENE–LEWIS DONOR MOLECULAR ASSOCIATIONS

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SUMMARY

Gas–liquid chromatography was used to study molecular associations involving 1-iodo-1-dodecyne and 21 Lewis donors. The data sometimes show slight positive or negative deviations from the diachoric model of solutions but they agree fairly well with the latest developments of conventional theories. However, Purnell's classical simple relationship $K_{R(M)} = f(C_A)$ gives precise thermodynamic parameters of donor–acceptor complexations. The behaviour of 1-iodododecyne towards very different Lewis bases shows that the electrostatic contribution accounts for 13–80% of molecular interactions.

INTRODUCTION

Iodoalkynes are Lewis acids, so they form molecular associations with electron donors[1]. Interactions can be divided into electrostatic and covalent types. In particular, experimental data relating to charge transfer (CT) complexes between 1-iodo-1-dodecyne and various Lewis bases can be correlated using the so-called double scale equation proposed by Drago *et al.*[2]:

$$-\Delta H = E_A E_D + C_A C_D \qquad (1)$$

where E_A and E_D, C_A and C_D are the susceptibility of the acid and base, respectively, to undergo electrostatic and covalent interactions.

UV spectroscopy cannot be used owing to the difficulty in observing the CT band lying in the vacuum ultraviolet region and the strong absorption of the Lewis bases. In IR spectroscopy, the stretching frequency ν_{CI} lies near 400 cm^{-1} and its low molar absorptivity makes the study difficult. However, spectroscopic evidence for a 1:1 complex between 1-iodo-1-dodecyne and pyridine was provided by the splitting of the ν_{6a} band of pyridine: at a base concentration of 0.425 mole dm^{-3} in carbon tetrachloride and a 1-iodo-1-dodecyne concentration varying from 0 to 1.585 mole dm^{-3}, an isosbestic point was observed (Fig. 1). The corresponding equilibrium constant by Liptay's method[3] is 1.07 ± 0.30 mole dm^{-3}.

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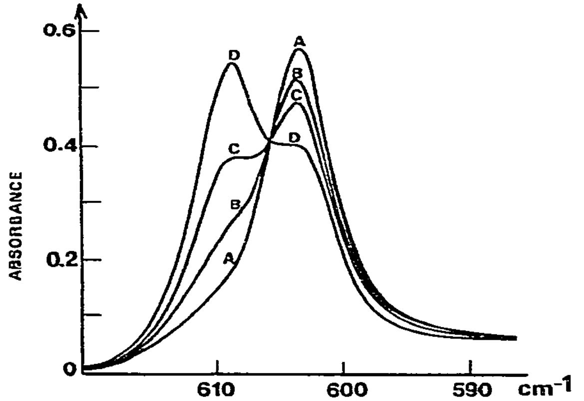


Fig. 1. ν_{6a} infrared band of pyridine in CCl_4. Pyridine concentration 0.425 mole dm^{-3}. 1-Iodo-1-dodecyne concentrations: 0, 0.277, 0.713 and 1.585 mole dm^{-3} for A, B, C and D, respectively.

We turned to gas–liquid chromatography, which has been used successfully by several workers[4–10] for the study of molecular associations; in our laboratory good agreement with the IR spectroscopic procedure was found as regards hydrogen-bonding associations between alkynes and proton acceptors[11].

A molecular interaction theory using a chromatographic procedure has recently been developed[12]. In this work an attempt has been made to check its ability to separate specific from non-specific interactions in donor–acceptor associations.

EXPERIMENTAL

Materials

We prepared 1-iodo-1-dodecyne (A) using Shostakovskii *et al.*'s method[13] from commercial 1-dodecyne and purified it by fractional distillation. Its low vapour pressure enabled us to use it as a liquid stationary phase below 80°C (P_0 = 0.1 mmHg).

The solvent squalane (S) was free from ethylenic hydrocarbons. Iodododecane, the reference liquid for Martire and Riedl's method[8] and the injected base solutes (D) were commercial products and were used without further purification. Table I gives the boiling points (T_b), the saturation vapour pressures (P_0), the molar volumes (V_D) and the second virial coefficients (B_{DD}) of the solutes. Saturation vapour pressures were calculated from literature data[14,15] and second virial coefficients from Berthelot's relationship from critical temperatures and pressures.

The densities of mixtures of iodododecyne and squalane and of pure liquids were evaluated using pyknometry (Table II). There is no excess volume of mixing:

$$V_M = V_S x_S + V_A x_A \qquad (2)$$

where x_i is the molar fraction of component i and V_i is the molar volume.

Apparatus and procedure

We used the injector and katharometer of a Girdel 3000 apparatus. Stainless-

TABLE I

PHYSICAL CONSTANTS OF BASES

Base	T_b^{760}	P_0 *(25°C)*	B_{DD} *(cm³)*	V_D *(cm³)*
Pyridine	115.5	20.7	1280.7	97.82
Propionitrile	97	46.7	1616	70.90
Dioxane	101	40.6	1468	85.71
Tetrahydrofuran	66	176	1138	80.63
Diethyl sulphide	92.1	58.4	1829	108.5
Diethyl selenide	110	31	–	111.4
Acetone	56.2	229.2	1024.9	74.0
2-Butanone	80	100	1292.1	90.1
3-Methyl-2-butanone	93	62.25	–	107.9
Chloroacetone	119	20	–	80.5
Butadione	88	79.7	–	87.0
Trifluoroacetone	22	–	–	–
Ethyl acetate	77	94.5	1396.2	98.3
Methyl acetate	57.5	216.2	1032.1	79.9
Ethyl thioacetate	116	23.6	–	106.6
Ethyl propionate	97	51.3	1817.2	115.7
Acetaldehyde	21	900.7	562.2	57.11
Diethyl ether	34.6	534.2	1046.0	104.75
Furan	31	614	–	73.11
Benzene	80	95.2	1378.8	89.4
Thiophene	84	87.7	–	79.47

steel columns (1 m × 2.2 mm I.D.) were placed in a liquid bath thermoregulated to within ±0.05°C. A mercury manometer measured the inlet pressure, about 300 mmHg above atmospheric pressure.

The flow-rate of the carrier gas (helium) (*ca.* 20 cm^3 min^{-1}) was measured with a soap film flowmeter. The pressure drop and the flow-rate were approximately constant for the 22 columns used.

The lack of a mixed second virial coefficient for the solute D and the carrier gas, B_{DHe}, prevented us from calculating the correction for zero pressure drop to obtain K_R^0, partition coefficient at zero total pressure. Indeed, corrections are not important; at 25°C in pure squalane, K_R, the partition coefficient at the column

TABLE II

DENSITIES OF 1-IODODODECYNE–SQUALANE MIXTURES AT FIVE TEMPERATURES

x*	*Density (g cm^{-3})*				
	15°C	*25°C*	*35°C*	*45°C*	*55°C*
0	0.8150	0.8093	0.8023	0.7960	0.7890
0.189	0.8574	0.8514	0.8440	0.8367	0.8295
0.503	0.9550	0.9480	0.9406	0.9329	0.9249
1	1.2660	1.2555	1.2450	1.2345	1.2242

* x = Molar fraction of iodododecyne.

pressure for benzene, is 525.3 and a value of 524.7 was derived from the correction using the equation[16]

$$\mathrm{Ln}\ V_\mathrm{N} = \ln K_\mathrm{R}^0 V_1 + \frac{2\ B_\mathrm{DHe} - V_\mathrm{D}^\infty}{RT} \cdot P_0 J_3^{\,4} \tag{3}$$

where V_N is the net retention volume, V_1 the volume of liquid phase in the column, V_D^∞ the partial molar volume of solute D at infinite dilution in the liquid phase, P_0 the column outlet pressure, R the gas constant, T (°K) the column temperature and

$$J_3^{\,4} = \frac{3\left(\dfrac{P_\mathrm{i}}{P_0}\right)^3 - 1}{4\left(\dfrac{P_i}{P_0}\right)^4 - 1}$$

where P_i is the column inlet pressure.

The support was Chromosorb P, acid washed, DMCS treated (60–80 mesh). The stationary phase was dissolved in dichloroethane and the solvent evaporated in a rotary dryer under a weak vacuum. The total mass of packing was determined by weighing and weight-percent of solvent mixture by ashing.

The contributions of solid and liquid interfaces to the partition coefficient were obtained from 10, 20 and 40% loadings (10, 20 or 40 g of liquid and 100 g of solid support). The loadings, molar and volume fractions and concentrations for each column are listed in Table III.

Measurements were made with triple injections of *ca.* 0.1 μl of liquids using a minimal attenuation katharometer. Infinite dilution of solute D in the stationary phase was derived from the variation in sample size and extrapolation to zero. Peaks were generally symmetrical, sometimes including weak tailing (Langmuir-type distribution). We computed the retention times using Conder and Young's procedure[17]; no significant variation of K_R *versus* $1/V_1$ was observed, except for the pure squalane column at 10% loading; solid–liquid interface adsorption was not taken into account[18].

TABLE III

COLUMN CHARACTERISTICS

x_A	C_A (*mole dm*$^{-3}$)	φ_A	*L = 10%*	*L = 20%*	*L = 40%*
0	0	0	×*	×	×
0.1195	0.245	0.057		×	×
0.1894	0.405	0.0943		×	×
0.265	0.5947	0.1384	×	×	×
0.328	0.766	0.1784		×	×
0.503	1.338	0.3114	×	×	×
0.690	2.143	0.4988		×	×
0.8995	3.436	0.7995		×	×
1	4.2967	1	×	×	×

* × = Existing column.

METHODS FOR CALCULATING EQUILIBRIUM CONSTANTS

K_R and γ_D^∞ were computed by the classical relationships

$$K_R = \frac{V_N}{V_1}$$

and

$$\gamma_D^\infty = \frac{nRT}{P_0 V_N} \cdot \exp\left(-\frac{B_{DD} - V_D}{RT} \cdot P_0\right) \tag{4}$$

We used four methods for calculating the equilibrium constant, the first proposed by Purnell[4], the latest by Harbison *et al.*[12], another method given by Eon *et al.*[9] improving Purnell's, and a simpler method by Martire and Riedl[8] using a reference compound.

Purnell's classical method[4]

The formation of a 1:1 complex between a volatile solute D and an involatile additive A in solution in an inert solvent S produces a change in the partition coefficient, as shown by Purnell[4]:

$$K_{R(M)} = K_{R(S)}\,(1 + K_c C_A) \tag{5}$$

where $K_{R(M)}$ is the partition coefficient for solute D between the mixed liquid phase (M = S + A) and the gas phase, $K_{R(S)}$ is the same coefficient in the pure solvent and K_c is the formation constant of complex AD in the mixed solvent.

Method of Harbison et al.[12]

In studying solute–alkane and solute–binary mixed alkane systems, Laub *et al.*[20] used Prigogine's treatment as modified by Janini and Martire[21] to calculate partition and activity coefficients. Harbison *et al.*[12] extended this study to ternary systems between aliphatic, acyclic and aromatic solutes and squalane–dinonyl phthalate solvent. First, for ternary systems without molecular association, they obtained

$$\ln K_{R(M)} = \ln K_{R(S)} + \left[\left(\frac{V_D}{V_A} - \frac{V_D}{V_S}\right) + \left(\chi_S^D - \chi_A^D + \frac{V_D}{V_A} \cdot \chi_S^A\right)\right] \varphi_A - \frac{V_D}{V_A} \cdot \chi_S^A \varphi_A^2 \tag{6}$$

where χ_j^i is the Flory-type interaction parameter between *i* and *j* and φ_A is the volume fraction of additive/acceptor A.

Eqn. 6 can be written as

$$\ln K_{R(M)} = U + V\varphi_A + W\varphi_A^2$$

For alkanes, U, V and W are found by a polynominal regression[22], so χ_S^A, independent of solute D, is known. Then, when only 1:1 complexes are present in ternary systems, a rigorous treatment gives the following equation:

$$\ln K_{R(M)} = \ln K_{R(S)} + \left[\left(\frac{V_D}{V_A} - \frac{V_D}{V_S}\right) + \chi_S^D - \chi_A'^D\right] \varphi_A + \\ + \frac{V_D}{V_A} \cdot \chi_S^A \, \varphi_A \varphi_S + \ln\left(1 + \frac{K_c}{V_A} \cdot \varphi_A\right) \quad (7)$$

$\chi_A'^D$ is the non-complexing component of interaction between D and A. Eqn. 7 can be rearranged to give

$$\ln K_{R(M)} - \chi_S^A \cdot \frac{V_D}{V_S} \varphi_A \varphi_S = r + s\varphi_A + \ln(1 + t\varphi_A) \quad (8)$$

where $r = \ln K_{R(S)}$, $s = (V_D/V_A - V_D/V_S) + \chi_S^D - \chi_A'^D$ and $t = (K_c/C_A)$. For each φ_A, the left-hand side of eqn. 8 is known; r, s and t can be calculated by the weighted non-linear least-squares method[22] and χ_S^D, $\chi_A'^D$ and K_c thus obtained.

Martire and Riedl's method[8]

From the equilibrium D + A ⇆ AD between a volatile solute D and A giving rise to the thermodynamic constant K:

$$K = \frac{[AD]}{[A]\,[D]}$$

Martire and Riedl derived

$$K' + 1 = \frac{V_{gA}^D \, V_{gR}^{al}}{V_{gR}^D \, V_{gA}^{al}} \quad (9)$$

where $K' = K[A] = K\gamma_A C_A$, V_{gj}^i is the specific retention volume of an injected solute i in liquid phase j, al represents alkane and R is the reference stationary liquid phase. γ_A was obtained from

$$\gamma_A = \frac{V_{gA}^{al} M_A}{V_{gR}^{al} M_R} \quad (10)$$

where M_i is the molecular weight of i.

Iodododecane was chosen as the reference stationary phase owing to its similarity to 1-iodododecyne as regards molecular size and polarizability. According to eqn. 9, only four specific retention volumes are needed in order to obtain K.

Eon et al.'s method[9]

Eqn. 5 takes into account neither the size differences between molecules nor the activity coefficients of A, S and D. Eon *et al.*[23] established the relationship

$$K_{R(M)} [V_S + (V_A - V_S)\, x_A] = V_S K_{R(S)} [1 - (\psi + K_x^*)\, x_A] \quad (11)$$

with

$$\psi = \frac{\gamma_{D(S)}^{\infty a}}{\gamma_{D(A)}^{\infty a}} \approx \frac{V_A}{V_S}\left[\frac{\exp\left(\dfrac{V_D}{V_A}\right)}{\exp\left(\dfrac{V_D}{V_S}\right)} - 1\right]$$

where $\gamma_{D(S)}^{\infty a}$ and $\gamma_{D(A)}^{\infty a}$, from Flory–Huggins theory, are athermal activity coefficients at infinite dilution for D in S and A, respectively; the standard state is pure liquid D. K_x^* is the thermodynamic constant:

$$K_x^* = \frac{x_{AD}}{x_A x_D} \cdot \frac{\gamma_{AD}^*}{\gamma_A^* \gamma_D^*}$$

where γ_i^* is the activity of species i with a reference state of infinite dilution.

Eqns. 2, 5 and 11 can be combined to give[24,25]

$$K_x^* = \frac{K_C}{v_S} + \frac{V_A}{V_S}\left[1 - \frac{\exp\left(\dfrac{V_D}{V_A}\right)}{\exp\left(\dfrac{V_D}{V_S}\right)}\right] \tag{12}$$

RESULTS AND DISCUSSION

Equilibrium constants and enthalpy variations

The value of $K_{R(S)}$ in pure squalane, $K_{R(A)}$ in pure iodododecyne and γ_D^{∞} at 25°C are given in Table IV. The $K_{R(M)}$ values were too numerous to be listed. As shown by a good correlation coefficient, varying from 0.97 to 0.998 for nine points, a linear relationship occurs between $K_{R(M)}$ and C_A for all bases. Nevertheless, it is worth noting that such a correlation coefficient may sometimes be found even if the data obey the following polynominal equation:

$$K_{R(M)} = U + VC_A + WC_A^{\,2}$$

where U, V, W are numerical parameters. For instance, for diethyl sulphide, in spite of the linear correlation coefficient of 0.995, the experimental data are better fitted by a parabolic regression. The inclusion of an extra power in C_A effects a reduction Δ in the sum of squares about the regression relative to the s^2 estimate. A suitable statistical test[26] for establishing whether or not this improvement is significant was then applied:

$$T = (n - m - 1)\cdot\frac{\Delta}{(\Sigma W_i D_i^{\,2})_{m+1}}$$

TABLE IV

PARTITION AND ACTIVITY COEFFICIENTS IN PURE LIQUIDS AT 25°C

Solute	$K_{R(S)}$*	$K_{R(A)}$*	$\gamma^{\infty}_{D(S)}$	$\gamma^{\infty}_{D(A)}$
Propionitrile	108.7	573.1	6.045	2.990
Dioxane	631.4	3191.1	1.418	0.597
Tetrahydrofuran	320.2	1250.7	0.641	0.361
Diethyl sulphide	754	3054	0.760	0.435
Diethyl selenide	1550	7103	0.740	0.362
Acetone	49.9	255	3.057	1.377
2-Butanone	177.3	772.2	2.022	0.997
3-Methyl-2-butanone	365.4	1472	1.43	0.872
Chloroacetone	393.1	1528	4.32	2.613
Butadione	160.8	524.6	2.051	1.910
Trifluoroacetone	10.1	16.4	—	—
Ethyl acetate	218.6	750.4	1.726	1.128
Methyl acetate	81.1	281.7	2.044	1.326
Ethyl thioacetate	1450	4517	1.026	0.749
Ethyl propionate	690.1	2120.1	1.007	0.734
Acetaldehyde	17.75	60.7	1.966	1.500
Diethyl ether	90.7	207.6	0.746	0.734
Furan	70.15	121.4	0.826	1.071
Benzene	525.3	983.5	0.699	0.839
Thiophene	541.4	1114.7	0.700	0.817
Pentane	114.4	105.6	0.624	1.521
Hexane	383.3	324.4	0.645	1.562
Heptane	1119.2	1024	0.699	1.633

* Confidence limits between 1 and 2%.

where n is the number of points and $\Delta = (\Sigma W_i D_i^2)_m - (\Sigma W_i D_i^2)_{m+1}$, where $(\Sigma W_i D_i^2)_m$ and $(\Sigma W_i D_i^2)_{m+1}$ are the weighted sum of the square of the residuals for m and $(m + 1)$ parameters, respectively.

For diethyl sulphide, the hypothesis $W = 0$ may be rejected at the 0.05 confidence level because $T = 33.78 > F_{1,4,0.05} = 7.71$ (seven points). Benzene, thiophene, diethyl ether, diethyl selenide and dioxane showed a similar behaviour; for acetaldehyde, tetrahydrofuran and propionitrile $T \approx F$, but for ketones and esters the rejection of the hypothesis outlined above is more significant and the linear relation was accepted without restriction.

We calculated K_c to a first approximation by the linear regression of eqn. 5. Table V contains equilibrium constants, ΔH determined by the linear least-squares fitting of log K_c *versus* $1/T$ and ΔS. Confidence limits for K_c are about 4%.

A rigorous study carried out by Martire and coworkers[27–29] showed that the found value of the equilibrium constant includes α, induced by non-complexing AD interactions or contact pairing. Hence K_c in eqn. 5 is overestimated.

To a second approximation we may infer, for reasons outlined above, that non-specific interactions involving iodododecane or iodododecyne and Lewis bases are similar. With a column of pure squalane and another column of pure iodododecane α', the interaction between iodododecane and a base, was evaluated approximately by eqn. 5. Removing α' from K_c we obtained the values given in Table VI.

TABLE V

RESULTS BY PURNELL'S METHOD FOR EQUILIBRIUM CONSTANTS, ΔH, ΔG AND ΔS

Base	K_c *(mol dm^{-3})**					$-\Delta H$ *(kcal mole^{-1})*	$s_{\Delta H}$** *(kcal mole^{-1})*	ΔG *(cal)*	$-\Delta S$ *(e.u.)*
	15°C	*25°C*	*35°C*	*45°C*	*55°C*				
Pyridine	3.42***	2.63***	2.05	1.63	1.30	4.6	0.3	−575	15.4
Propionitrile	1.17	1.06	0.87	0.77	0.66	2.8	0.15	−35	9.3
Dioxane	1.24	1.04	0.78	0.67	0.57	3.7	0.2	−23	12.3
Tetrahydrofuran	0.91	0.72	0.57	0.51	0.40	3.7	0.2	196	13.1
Diethyl sulphide	0.88	0.72	0.59	0.50	0.42	3.5	0.2	230	12.5
Diethyl selenide	1.03***	0.84	0.69	0.58	0.49	3.5	0.3	104	12.1
Acetone	1.10	0.94	0.79	0.67	0.60	2.95	0.1	37	10.0
2-Butanone	0.93	0.73	0.63	0.56	0.50	2.9	0.2	190	10.2
3-Methyl-2-butanone	0.90	0.67	0.55	0.51	0.45	3.15	0.2	238	11.4
Chloroacetone	0.78	0.65	0.58	0.51	0.49	2.2	0.2	257	8.4
Butadione	0.66	0.54	0.48	0.43	0.40	2.5	0.2	389	9.0
Trifluoroacetone	0.15	0.145	0.14	0.135***	0.13***	0.65	0.1	1150	5.9
Ethyl acetate	0.65	0.55	0.48	0.45	0.38	2.5	0.15	356	9.6
Methyl acetate	0.63	0.54	0.47	0.43	0.39	2.3	0.1	367	9.0
Ethyl thioacetate	0.64	0.55	0.44	0.42	0.37	2.5	0.15	356	9.6
Ethyl propionate	0.58	0.52	0.45	0.40	0.36	2.2	0.1	389	9.0
Acetaldehyde	0.47	0.44	0.36	0.30	0.25	3.1	0.2	489	12.0
Diethyl ether	0.33	0.29	0.24	0.21	0.18	2.9	0.1	737	12.2
Furan	0.18	0.17	0.14	0.13	0.12	1.7	0.2	1056	9.2
Benzene	0.22	0.205	0.19	0.18	0.165	1.4	0.2	944	7.9
Thiophene	0.23	0.21	0.19	0.17***	0.16***	1.8	0.3	826	9.1

* Confidence limits 4%.

** Standard deviation to linear regression.

*** Extrapolated values.

TABLE VI

$K_c - \alpha'$ VALUES AND CORRESPONDING ΔH VALUES

Base	$K_c - \alpha'$ *(mole dm^{-3})**				$-\Delta H$ *(kcal mol^{-1})*	$s_{\Delta H}$** *(kcal mol^{-1})*
	15°C	*25°C*	*35°C*	*55°C*		
Propionitrile	0.63	0.59	0.48	0.39***	2.4	0.3
Dioxane	0.946	0.763	0.529	0.363	4.6	0.4
Tetrahydrofuran	0.726	0.530	0.40	0.28	4.5	0.3
Diethyl sulphide	0.667	0.494	0.389	0.28	4.05	0.3
Diethyl selenide	0.81***	0.590	0.47	0.31	4.2	0.4
Acetone	0.795	0.678	0.508	0.39	3.5	0.3
2-Butanone	0.58	0.427	0.345	0.262	3.6	0.4
3-Methyl-2-butanone	0.435	0.36	0.30	0.213	3.4	0.2
Chloroacetone	0.335	0.27	0.22	0.156	3.6	0.2
Butadione	0.317	0.267	0.19	0.16	3.4	0.4
Ethyl acetate	0.41	0.335	0.28	0.20	3.05	0.2
Methyl acetate	0.39	0.322	0.27	0.19	2.9	0.2
Ethyl thioacetate	0.402	0.335	0.235	0.20	3.15	0.3
Ethyl propionate	0.343	0.304	0.252	0.187	2.9	0.2
Acetaldehyde	0.23	0.19	0.16	0.11	3.5	0.2
Diethyl ether	0.22	0.185	0.15	0.10	3.8	0.2

* Confidence limits 6–8%.

** Standard deviation to linear regression.

*** Extrapolated values.

TABLE VII

RESULTS OF MARTIRE AND RIEDL'S METHOD FOR K AND ΔH

Base	K (*mole dm*$^{-3}$)				$-\Delta H$ (*kcal mol*$^{-1}$)	$s_{\Delta H}$** (*kcal mole*$^{-1}$)
	15°C	*25 C*	*35°C*	*55 C*		
Propionitrile	0.291	0.236	0.208	0.161	2.7	0.15
Dioxane	0.529	0.475	0.425	0.296	2.8	0.3
Tetrahydrofuran	0.454	0.385	0.325	0.235	3.1	0.3
Diethyl sulphide	0.393	0.354	0.347	0.283	3.2	0.2
Diethyl selenide		0.373	0.312	0.225	3.3	0.2
Acetone	0.402	0.314	0.275	0.234	2.5	0.2
2-Butanone	0.362	0.275	0.254	0.202	2.6	0.2
3-Methyl-2-butanone	0.351	0.274	0.249	0.191	2.8	0.2
Chloroacetone	0.191	0.175	0.146	0.134	1.8	0.3
Butadione	0.237	0.195	0.175	0.137	2.5	0.15
Trifluoroacetone		0.048	0.043	0.040	~0	
Ethyl acetate	0.29	0.262	0.22	0.17	2.3	0.15
Methyl acetate	0.287	0.252	0.222	0.177	2.2	0.10
Ethyl thioacetate	0.23	0.207	0.17	0.14	2.2	0.15
Ethyl propionate	0.301	0.244	0.221	0.183	2.3	0.15
Acetaldehyde	0.28	0.24	0.205		2.8	0.1
Diethyl ether	0.24	0.204	0.178		2.7	0.1
Furan	0.061	0.060	0.055	0.051	0.8	0.2
Benzene	0.054	0.050	0.047	0.042	1.1	0.2
Thiophene	0.072	0.070	0.062	0.045	1.2	0.2

* Confidence limits 4%.

** Standard deviation to linear regression.

TABLE VIII

RESULTS OF EON *et al.*'s METHOD FOR K_x^* AND ΔH

Base	K_x^* *(molar fraction)**					$-\Delta H$ *(kcal mole^{-1})*	$s_{\Delta H}$** *(kcal mol^{-1})*
	15°C	*25°C*	*35°C*	*45°C*	*55°C*		
Pyridine	6.52***	4.94***	3.80	2.97	2.33	4.95	0.2
Propionitrile	2.18	1.95	1.57	1.365	1.15	3.1	0.2
Dioxane	2.30	1.89	1.38	1.16	0.96	4.2	0.2
Tetrahydrofuran	1.67	1.28	0.99	0.865	0.65	4.3	0.2
Diethyl sulphide	1.57	1.25	0.99	0.81	0.65	4.15	0.1
Diethyl selenide	1.86***	1.47	1.175	0.955	0.78	4.1	0.1
Acetone	2.04	1.71	1.415	1.17	1.03	3.3	0.1
2-Butanone	1.69	1.29	1.09	0.95	0.82	3.3	0.2
3-Methyl-2-butanone	1.61	1.15	0.91	0.83	0.71	3.7	0.4
Chloroacetone	1.41	1.15	1.00	0.86	0.82	2.6	0.2
Butadione	1.17	0.93	0.81	0.70	0.64	2.85	0.2
Ethyl acetate	1.14	0.91	0.79	0.73	0.59	2.9	0.2
Methyl acetate	1.13	0.94	0.80	0.715	0.63	2.75	0.1
Ethyl thioacetate	1.11	0.92	0.71	0.66	0.56	3.2	0.3
Ethyl propionate	0.98	0.85	0.71	0.61	0.52	3.0	0.1
Acetaldehyde	0.845	0.78	0.62	0.50	0.40	3.65	0.3
Diethyl ether	0.51	0.43	0.33	0.27	0.21	4.3	0.3
Furan	0.26	0.24	0.18	0.16	0.135	3.2	0.3
Benzene	0.32	0.28	0.25	0.23	0.20	2.1	0.3
Thiophene	0.35	0.31	0.27	0.22***	0.20***	2.7	0.4

* Confidence limits 4%.

** Standard deviation to linear regression.

*** Extrapolated values.

The values of K, $K_x^\ddagger$ and ΔH calculated by Martire and Riedl's and Eon *et al.*'s methods are listed in Tables VII and VIII. Comparison with Tables V and VII showed that the ΔH deviations were not significant. Martire and Riedl's method yielded values 0.3–0.5 kcal smaller and Eon *et al.*'s 0.5–0.7 kcal higher than Purnell's. These differences are linked with the nature of equilibrium constants: Martire and Riedl's constants are true thermodynamic ones, Eon *et al.*'s constants are thermodynamic ones in a given solvent and Purnell's constants are based on a concentration scale.

Using Harbison *et al.*'s process applied to pentane, hexane and heptane (eqn. 6), we found a mean value of 0.550 for χ_S^A. Including this value in eqn. 8, we obtained r, s and t by a weighted least-squares method. Corresponding χ_S^D, $\chi_A'^D$ and K_c values are listed in Table IX.

χ_S^D and $\chi_A'^D$ were about the same: in general, bases induced similar non-complexing interactions with iodododecyne and squalane. This result agrees with chemical theory and makes this method viable. On the other hand, χ_R^D (R = iodododecane) calculated from the equation

$$\ln \gamma_{D(R)}^{\infty} = \ln \frac{V_D}{V_R} + \left(1 - \frac{V_D}{V_R}\right) + \chi_R^D \qquad (13)$$

was different to χ_S^D, making the previous approximation $\alpha' = \alpha$ wrong. Hence the corrected values of K in Table VI are smaller than the true values. Comparison of Tables V and IX showed reasonable agreement between K_c values.

It is worth noting that all methods gave the same basicity scale and similar values of C_A and E_A, Drago *et al.*'s acid parameters, and in particular, the same C_A/E_A ratio (see below). Hence our results are consistent.

Theoretically, Harbison *et al.*'s method yields better values of K_c because it takes into account interactions between all molecules present. Eon *et al.*'s method allows the disturbing effects of the size differences between the molecules to be suppressed: at 25°C, the correction term in eqn. 12 varies from -0.065 to -0.135 for $K_x^\ddagger$ varying from 0.4 to 5.

In Martire and Riedl's method, great care must be taken with the choice of the reference solvent: the molecular polarizability, size and shape should be the same as those of the electron donor, as far as possible. No specific interaction must be observed between this reference compound and D.

The mathematical treatment, fitting through polynomial eqns. 6 and 8, as described for Harbison *et al.*'s method, requires more numerous and more accurate experimental data than other methods. In this work, in spite of the many columns used, the too large standard deviations of K_c and the too narrow temperature interval induced ΔH values with a bad confidence level.

Comparison with literature data

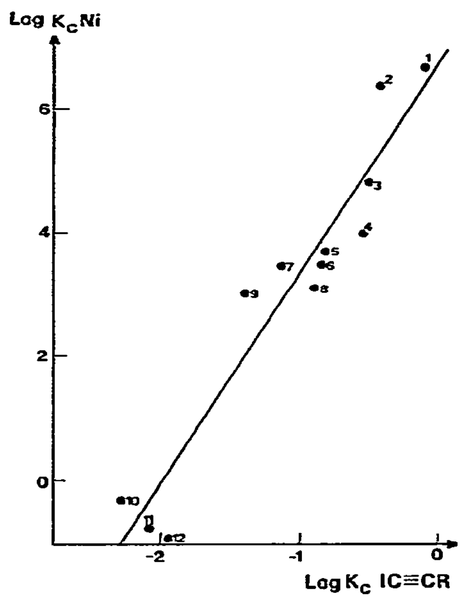
Our χ values are very similar to the literature data[12,30] (Table VII). By a simple chromatographic device, not very different from that of Purnell's, Schurig *et al.*[31] obtained equilibrium constants for 38 bases (12 of which were common to ours) with a Lewis acid, the dimeric 3-fluoroacetylcamphorate nickel(II), that was much stronger than iodododecyne, as shown by the K_c values (K = 782.9 at 75°C and 1.04 at 25°C

TABLE IX

RESULTS OF HARBISON *et al.*'s METHOD AT 25°C FOR χ PARAMETERS AND K_c

Solute	χ_S^D	χ_S^D	$\chi_A'^D$	χ_R^D	K_c *(mole dm^{-3})*	sK_c *(mole dm^{-3})*
Acetonitrile	3.76	3.53*	3.55	2.62	0.67	0.10
Propionitrile	3.10		3.07	2.08	0.79	0.10
Dioxane	1.326		1.12	0.75	0.58	0.05
Tetrahydrofuran	0.517		0.56	0.17	0.535	0.05
Diethyl sulphide	0.444		−0.116	0.145	0.145	0.05
Diethyl selenide	0.457		0.391	0.03	0.50	0.07
Acetone	2.20	2.14*	2.20	1.42	0.73	0.05
2-Butanone	1.536	1.55*	1.32	0.98	0.35	0.05
3-Methyl-2-butanone	1.142		1.16	0.66	0.40	0.04
Chloroacetone	2.476		2.48	1.72	0.14	0.10
Butadione	2.02		2.15	1.43	0.49	0.15
Ethyl acetate	1.37		1.32	0.90	0.345	0.02
Methyl acetate	1.68		1.44	1.15	0.25	0.05
Ethyl thioacetate	0.82		0.74	0.42	0.275	0.05
Ethyl propionate	0.736		0.98	0.40	0.46	0.03
Acetaldehyde	2.06		2.33	1.47	0.43	0.10
Diethyl ether	0.449		0.529	0.351	0.18	0.05
Benzene	0.558	0.536* 0.583**	0.711	0.236	0.16	0.05
Pentane	0.255	0.205* 0.246**	0.650	0.452	0	
Hexane	0.192	0.183* 0.187**	0.647	0.391	0	
Heptane	0.148	0.147* 0.149**	0.640	0.359	0	

* Ref. 25.
** Ref. 11.



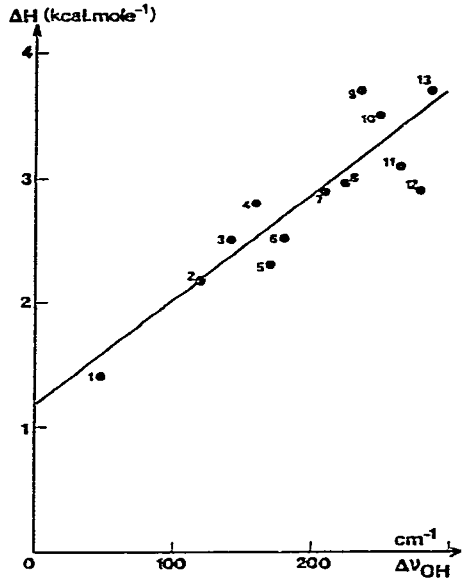


Fig. 2. ln K_c for base–dimeric 3-trifluoroacetylcamphorate of Ni(II) complexes at 75°C *versus* ln K_c for base–1-iodo-1-dodecyne complexes at 25°C. 1 = Dioxane; 2 = tetrahydrofuran; 3 = diethyl sulphide; 4 = 2-butanone; 5 = ethyl acetate; 6 = methyl acetate; 7 = acetaldehyde; 8 = ethyl propionate; 9 = diethyl ether; 10 = furan; 11 = benzene; 12 = thiophene.

Fig. 3. ΔH of base–1-iodo-1-dodecyne complexes *versus* $\Delta\nu_{OH}$ of phenol in CCl_4. 1 = Benzene; 2 = chloroacetone; 3 = butadione; 4 = propionitrile; 5 = methyl acetate; 6 = ethyl acetate; 7 = 2-butanone; 8 = acetone; 9 = dioxane; 10 = diethyl sulphide; 11 = acetaldehyde; 12 = diethyl ether; 13 = tetrahydrofuran.

with dioxane). Fig. 2 represents the comparison between log K_c [Ni(II)] at 75°C *versus* log K_c (iodododecyne) at 25°C, the correlation is satisfactory ($r = 0.93$). This result is surprising, because in nickel(II) complexes "non-specific" interactions are negligible in comparison with the so-called charge transfer forces: there is no basic difference in nature between strong and weak association of the bases under study.

Comparison of the basicity scale obtained with iodododecyne by gas–liquid chromatography and with phenol by IR spectroscopy (Fig. 3) is an argument in favour of the accuracy of our ΔH values. Some discrepancies for dioxane and diethyl ether may be noted.

Chromatography gives, for a large set of bases, association enthalpies with iodododecyne under rigorously similar conditions. Further, bases are at infinite dilution, and the volume fraction of acid in the non-polar solvent varies from 0 to 1.

Application of Drago et al.'s relationship to iodododecyne

For each set of enthalpies, we checked the two-parameters equation $-\Delta H = E_A E_D + C_A C_D$ for ten bases whose E_D and C_D parameters are known. We obtained similar E_A and C_A values for iodododecyne (Table X).

As shown in the graphical representation of $-\Delta H/E_D$ *versus* C_D/E_D (Fig. 4), diethyl sulphide and diethyl selenide are very important for the fitness of the corre-

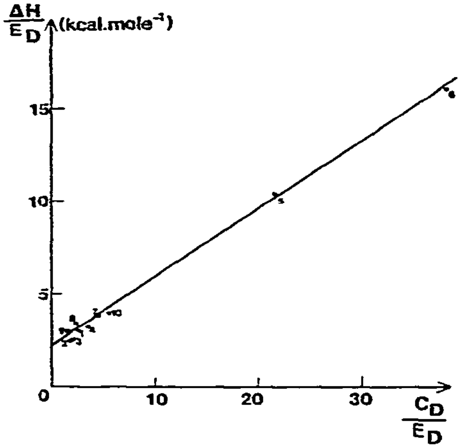


Fig. 4. $\Delta H/E_D$ *versus* C_D/E_D for base–1-iodo-1-dodecyne complexes. 1 = Acetone; 2 = ethyl acetate; 3 = methyl acetate; 4 = diethyl ether; 5 = diethyl sulphide; 6 = diethyl selenide; 7 = tetrahydrofuran; 8 = dioxane; 9 = benzene; 10 = pyridine.

lation ($r = 0.9987$). From E_A and C_A values and from their ratio we conclude that 1-iodododecyne is a less "soft" acid than iodine, according to the hard–soft acid–base (HSAB) principle of Pearson[32]. The contributions of electrostatic interactions to the enthalpy value are 13, 20, 50, 60, 70 and 80% for the associations of iodododecyne with diethyl selenide, diethyl sulphide, pyridine, ethers, ketones and esters, respectively.

Moreover, for carbonyl bases, the treatment of the data for variation of log K_c with $1/T$ shows that thermodynamic parameters are controlled by a linear free-energy relationship (LFER) with infinite β (isoenthalpic family)[33,34].

TABLE X

C_A AND E_A PARAMETERS OF DRAGO *et al.*'s EQUATION

Constant method	C_A	s_{C_A}*	E_A	s_{E_A}*	$\frac{C}{A}$	r**
Purnell	0.364	0.040	2.102	0.129	0.17	0.964
$K_c + \alpha - \alpha'$	0.416	0.076	2.571	0.198	0.16	0.937
Martire and Riedl	0.336	0.013	1.778	0.062	0.19	0.983
Eon *et al.*	0.418	0.086	2.521	0.214	0.17	0.932

* Standard deviation of the regression.
** Correlation coefficient.

Applicability of the diachoric solutions relationship

Purnell, Laub and co-workers[35–37] found that the equation

$$K_{R(M)} = K_{R(S)}\varphi_S + K_{R(A)}\varphi_A \tag{12}$$

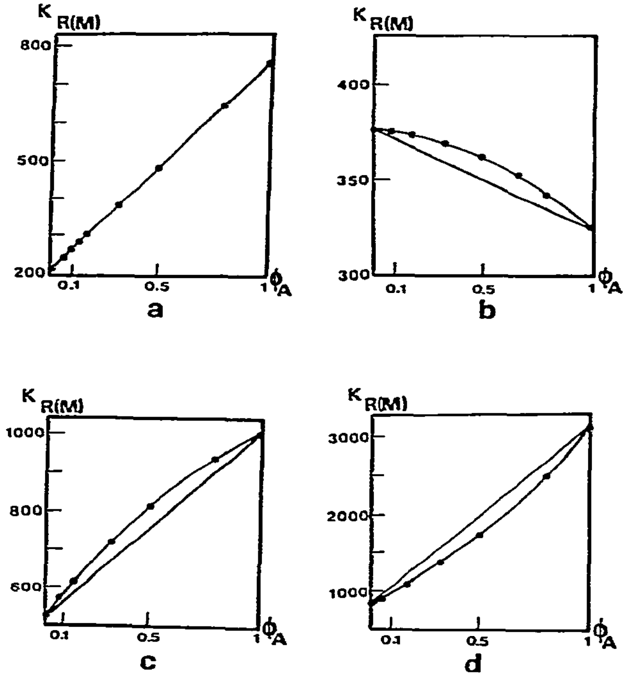


Fig. 5. Plots of $K_{R(M)}$ at 25°C *versus* φ_A. (a) Ethyl acetate; (b) hexane; (c) benzene; (d) diethyl sulphide.

is often obeyed for many chromatographic systems that they called diachoric. In fact, similarities can be found with eqn. 5 because $\varphi_A = V_A C_A$.

For iodododecyne–base–squalane systems we observed four types of curves for eqn. 12 (Fig. 5):

Type a: straight lines with 2% maximum deviations for ketones, esters and tetrahydrofuran.

Type b: curves with positive deviations and $K_{R(A)} < K_{R(S)}$ for alkanes.

Type c: curves with positive deviations and $K_{R(A)} > K_{R(S)}$ for acetaldehyde (weak deviation), benzene, thiophene and diethyl ether.

Type d: curves with negative deviations and $K_{R(A)} > K_{R(S)}$ for propionitrile (weak deviation), dioxane, diethyl sulphide and diethyl selenide.

As did Harbison *et al.*[12], we also noticed two possibilities:

(i) Eqns. 6 and 7 from conventional theories of solutions are well adapted to explain the results. In this instance, the diachoric relationship cannot be applied to all systems and deviations depend on relative values of the three parameters χ_S^D, $\chi_A'^D$ and χ_S^A.

(ii) The diachoric hypothesis is always applicable: in this instance an explanation must be found for the experimental deviations listed above, but this is difficult. One reason for the divergence is the dimerization of iodododecyne and another is the existence of 1:2 complexes.

We chose the first possibility and our K_c and ΔH values agree very well with it. However, we must bear in mind that in our study diachoric linearity is observed for about 50% of bases and, moreover, when deviations occur, they never exceed 4%.

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