The Extractability of Potassium as Picrates (KPic and K(L)Pic, L: 18-Crown-6) and Its Relationship to the Properties of the Solvents

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The distribution ratios, D, of potassium between an aqueous KCl solution and 57 organic solvents (8 alcohols, 12 ketones, 6 esters, 3 ethers, and 28 hydrocarbons (24 halo- and 2 nitro-substituted and 2 unsubstituted)) were determined in the presence or in the absence of L. The presence of L markedly enhances the extractability of potassium when the halogenated hydrocarbon solvents are used, but only a slight enhancement can be observed for the oxygen-containing solvents. Among the properties showing good correlations with D, Hansen's three-dimensional solubility parameters and Dimroth's E_T values are most satisfactory for their applicability to a wide variety of solvents.

Potassium picrate in an aqueous solution can be extracted only when a highly polar substance is used as a solvent. Most such solvents are miscible with water; hence, only a limited number of water-immiscible solvents can be used.

L is a well-known ligand of the endopolarophilic type, with the polar binding sites turned inside towards the cation and the lipophilic methylene groups turned outside. A wider variety of solvents, therefore, are made subjects of the extraction study of K(L)Pic because of its increased lipophilicity.

Although the knowledge of the polarity of a solvent is important in solvent-extraction chemistry, there are only a few reports which describe a quantitative relation between the extractability of the ion-pair and the polarity of the solvent.[1,2] In chelate-extraction systems, however, the solubility parameter of the solvent is known to have a close relationship with the extractability of the chelate.

This paper will describe how, besides the solubility parameter, the transition energy for a solvatochromic indicator can serve as a numerical polarity scale for the present extractions.

Experimental

Materials. Reagent-grade solvents (Tokyo Kasei Co., Ltd.) were washed with an aqueous sodium carbonate solution and then with water several times. The K(L)Pic was prepared by adding an equimolar amount of commercially available L (Nisso Co., Ltd.) to an aqueous KPic solution and was then recrystallized repeatedly from methanol.

Distribution Ratios. Aqueous picrate solutions (10^{-4} mol dm^{-3}) were prepared by dissolving each picrate in a solvent-saturated potassium hydrogencarbonate solution, the total potassium concentration being 10^{-2} mol dm^{-3}. Twenty milliliters of the aqueous solution and an equal volume of a water-saturated solvent were transferred to a 50-cm^3 centrifuge tube. After being shielded tightly, the vessel was immersed in a water bath thermostated at (25±0.01) °C and gently shaken for 1 h. The value of D was calculated from the aqueous picrate concentration, as determined by the use of a Hitachi 124 spectrophotometer.

Water Miscibilities. The water content of the organic phase was determined in each distribution run by the use of a Mitsubishi Kasei CA-01 Karl-Fischer titrator.

Solubilities. The solubilities of the picrates in the water-saturated solvents at 25 °C were determined by means of HPLC (Shimadzu liquid chromatograph; column: 250 mm × 4 mm Zorbax PCH, mobile phase: methanol, detector: SPD-1 spectrophotometer).

Results and Discussion

D Values and Structures. The D values for oxygen-containing solvents are listed in Table 1, together with some other data.

Table 1 shows that the D value for benzyl alcohol is greater than that for 1-heptanol, though both have the same number of carbon atoms. Such a phenyl-substitution effect can also be seen with acetophenone, benzyl acetate, and probably anisole. The presence of double bonds also enhances the extractabilities of the picrates, as can be seen for mesityl oxide. Such is the case with allyl chloride, as will be seen later. The presentation of the D values on a logarithmic scale produces relatively simple relations with the number of carbon atoms, N, of the solvent molecule, as is shown in Fig. 1. It must

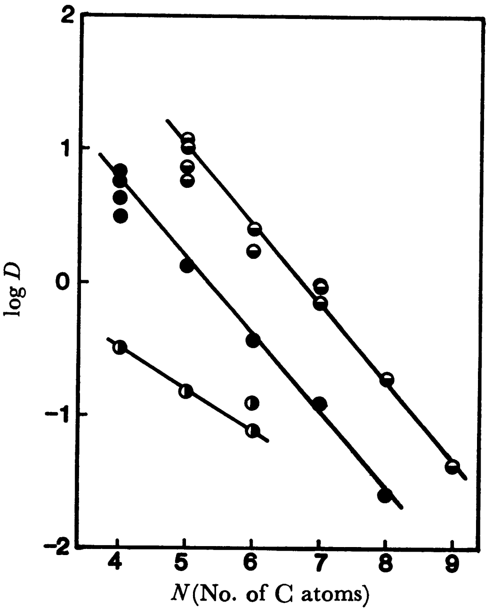

Fig. 1. Relation between log D for K(L)Pic and the number of carbon atoms of the solvent.
○: (Halogenated) hydrocarbons, ●: alcohols, ◒: ketones, ◑: esters, ◐: ethers.

Table 1. Distribution ratios of the picrates and some properties of oxygen-containing solvents

	Solvent	D		$10^4 s$ / mol dm^{-3}		$n(H_2O)$	δ[b]	δ_o[b]	δ_d[b]	δ_p[b]	δ_h[b]	V[c] / cm^3 mol^{-1}	E_T[d] / kcal mol^{-1}
		K(L)Pic	KPic	K(L)Pic	KPic		cal$^{1/2}$ cm$^{-3/2}$						
1	*n*-BuOH	6.7	6.79	67	105	0.507	11.4	11.3	7.8	2.8	7.7	91.5	50.2
2	*i*-BuOH	3.0	2.9	32	55	0.470	11.19					92.3	
3	*s*-BuOH	4.3	4.0	132	312	0.724	11.05	10.8	7.7	2.8	7.1	92	
4	*n*-$C_5H_{11}OH$	1.3	1.2	29.1	25.8	0.380	10.95	10.61	7.81	2.2	6.8	108.7	
5	*n*-$C_6H_{13}OH$	0.37	0.25	10	9.1	0.309	10.65					125.5	
6	*n*-$C_7H_{15}OH$	0.12	0.05	4.0	3.4	0.249	10.5					141.4	
7	*n*-$C_8H_{17}OH$	0.03	0.01	3.6	4.0	0.255	10.24	10.3	8.3	1.6	5.8	157.7	
8	$PhCH_2OH$	5.7	2.9	2130	78.0	0.384	12.05	11.6	9.0	3.1	6.7	103.6	50.8
9	*n*-PrCOMe	7.3	4.9	321	168	0.155	8.7					106.1	
10	Et_2CO	5.7	2.9	311	104	0.107	8.8	8.9	7.7	3.7	2.3	106.4	
11	*n*-BuCOMe	2.5	1.3	130	50	0.101						123.3	
12	*i*-BuCOMe	1.7	0.85	100	48.8	0.097	8.3	8.3	7.5	3.0	2.0	125.8	
13	Mesityl oxide[a]	10	6.1	390	215	0.155	9.2	9.2	8.0	3.5	3.0	115.6	
14	*n*-$C_5H_{11}COMe$	0.96	0.47	78	32.2	0.084	8.4					139.3	
15	*i*-$C_5H_{11}COMe$	0.92	0.47	69	31.9	0.083	8.4	8.5	7.8	2.8	2.0	142.8	
16	*n*-BuCOEt	0.69	0.27	59	15.5	0.057	8.3					139.6	
17	(*i*-Pr)$_2$CO	0.96	0.25	63	13.4	0.052	8.2					141.6	
18	*n*-$C_6H_{13}COMe$	0.19	0.11	41	18.2	0.068						156.6	
19	PhCOMe	11	4.9	1160	268	0.103	9.7	9.68	8.55	4.2	1.8	117.4	41.3
20	(*i*-Bu)$_2$CO	0.04	<0.001	8	2.2	0.033	8.4					167.9	
21	CH_3COOR, R=Et	0.32	0.27	52	70.2	0.132	8.6	9.1	7.44	2.6	4.5	98.5	38.1
22	CH_3COOR, *n*-Pr	0.15	0.11	32.4	29.9	0.097	8.4					115	
23	CH_3COOR, *n*-Bu	0.08	0.05	17	19.1	0.070	8.3	8.5	7.7	1.8	3.1	132.5	
24	CH_3COOR, $PhCH_2$	0.12	0.04	84	10.2	0.070	9.5					144.4	
25	PC[a]	99	99	1500	1220	0.318	13.3	13.3	9.8	8.8	2.0	85	46.6
26	TBP[a]	15.7	13.3	52	1200	0.534	7.7					272	33.9
27	Et_2O	0.01	<0.001	3.1	0	0.052	7.4	7.7	7.1	1.4	2.5	104.8	34.6
28	(*n*-Bu)$_2$CO	<0.001	<0.001	0.3	0	0.012	7.76					170.5	33.4
29	PhOMe	0.09	<0.001	177	0	0.012	9.9					108.7	37.2

a) PC=Propylene carbonate, TBP=tributyl phosphate, Mesityl oxide=4-methyl-3-pentene-2-one. b) Ref. 4. c) V=mol wt/density (density: Ref. 5). d) Ref. 6.

be noted that, in Fig. 1, modified N values are used for the phenyl-substituted ($N-3$) and double-bond-containing solvents ($N-1$), so that the best fit can be obtained. Among the solvents with the same number of carbon atoms, the extractabilities of K(L)Pic decrease in the following sequence: ketones>alcohols>esters>ethers. A quite similar plot is obtained for the extraction of KPic.

The D values for hydrocarbon solvents are listed in Table 2. No hydrocarbon solvents can extract KPic. Nitro-substituted ones show exceptionally high extractabilities both for KPic and K(L)Pic. It is obvious that the D values decrease with an increase in the number of the CH_2 units of the solvent: C_3H_7Cl, $C_4H_9Cl>C_5H_{11}Cl>C_6H_{13}Cl$. The double-bond containing solvents likewise show higher extractabilities than the corresponding saturated ones: allyl chloride>propyl chloride.

The extractability of K(L)Pic tends to decrease with an increase in the number of halogen atoms ($CH_2Cl_2>CHCl_3>CCl_4$, *o*-dichlorobenzene>chlorobenzene), and completely halogenated solvents, such as CCl_4 and $CBrCl_3$, do not show any appreciable extractabilities. The position of halogen atoms also has a significant influence, as can be seen for 1,1- and 1,2-dichloroethane, for example. It is noticeable that the extractability is greatly affected by the *cis*-*trans* isomerism (*cf.* 1,2-dichloroethylene).

The chlorinated solvents always show the highest extractability among the halogenated solvents, as is best shown in monohalogen derivatives of benzene.

Dielectric Constant, ε, and Dipole Moment, μ. The log D values tend to increase with ε, in accordance with Irving and Lewis' observation of the partition of indium chloride,[1)] though the correlation is far from satisfactory. Freiser also pointed out, for the distribution of tridodecylammonium perrhenate, that there isverylittle correlation between the logarithmic distribution constants and the ε values.[2)] The log D values also increase with μ, though the degree of correlation is much lower than that observed between log D and ε. It should, however, be noted that, among the solvent parameters investigated, only ε and μ show the expected low extractabilities of K(L)Pic into CCl_4 and *trans*-1,2-dichloroethylene.

Solubilities of the Picrates, s. The solubilities of the picrates in water-saturated solutions are shown in Tables 1 and 2. A log D *vs.* log s plot for K(L)Pic in the oxygen-containing solvents yields a straight line for

Table 2. Distribution ratios of the picrates and some properties of hydrocarbon solvents

	Solvent	D K(L)Pic	D KPic	$10^4 s$/mol dm^{-3} K(L)Pic	$10^4 s$/mol dm^{-3} KPic	$10^3 n(H_2O)$	δ	δ_o	δ_d	δ_p	δ_h	V/cm^3 mol^{-1}	E_T/kcal mol^{-1}
							cal$^{1/2}$ cm$^{-3/2}$						
30	CH_2Cl_2	1.13	<0.001	7240	0	7.8	9.7	9.9	8.9	3.1	3.0	63.9	41.1
31	$CHCl_3$	0.53	0	5270	0	5.7	9.3	9.3	8.7	1.5	2.8	80.7	39.1
32	CCl_4	<0.001	<0.001	490	0	0.9	8.6	8.7	8.7	0	0.3	97.1	32.5
33	CH_2Br_2	0.79	0.02			6.0						69.5	
34	$CHBr_3$	0.43	0.01			4.4	10.5					88	
35	CH_2BrCl	0.92	0.01			7.6						67.3	
36	$CHBrCl_2$	0.45	0.01			4.3						82.7	
37	$CBrCl_3$	<0.001	<0.001			1.1							
38	CH_2ClCH_2Cl	1.17	<0.001	1490	0	8.2	9.8	9.76	9.2	2.6	2.0	79.4	41.9
39	CH_3CHCl_2	0.23	<0.001			4.2	9.1	9.2	8.3	3.3	2.2	85	
40	CH_3CCl_3	0.05	<0.001			2.5	8.5					100	
41	ClCH=CHCl,*cis*-	0.67	0.03			5.8	9.7	8.7	7.8	3.8	1.0	76	
42	ClCH=CHCl,*trans*-	<0.001	<0.001			2.8	9					78	
43	*n*-PrCl	0.04	<0.001			2.7	8.5					88.3	
44	*i*-PrCl	0.05	<0.001			3.1						88	
45	CH_2=$CHCH_2Cl$	0.11	<0.001			6.2						81.5	
46	$CH_3CHClCH_2Cl$	0.16	<0.001			5.0						97.8	
47	*n*-BuCl	0.04	<0.001			2.3						104	
48	*n*-$C_5H_{11}Cl$	0.02	<0.001			2.1						121	
49	PhX, X=H	0.02	<0.001	33.9	0	2.84	9.2	9.1	9.0	0	1.0	89.4	34.5
50	PhX, X=F	0.09	<0.001			2.6						93.6	38.1
51	PhX, X=Cl	0.14	<0.001	113	0	2.7	9.5	9.6	9.3	2.1	1.0	102.1	37.5
52	PhX, X=Br	0.04	<0.001			2.1	9.87	10.6	10	2.7	2.0	105	37.5
53	PhX, X=I	0.03	<0.001			3.6						111	37.9
54	*o*-$PhCl_2$	0.27	<0.001	232	0	2.5	10	10	9.4	3.1	1.6	112.8	
55	$PhNO_2$	13.3	0.18	1130	3.64	14.9	11.1	10.9	9.8	4.2	2.0	102.7	42.0
56	$PhCH_3$	0.01	<0.001	13.4	0	2.68	8.93	8.9	8.8	0.7	1.0	106.8	33.9
57	*o*-$NO_2C_6H_4CH_3$	6.1	0.11	714	2.1	15.0						117.9	

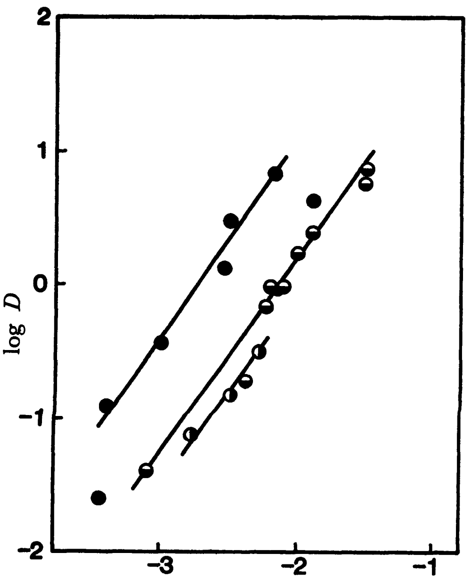

Fig. 2. Relation between log D for K(L)Pic and the solubility of the picrate in the solvent.
Symbols: see Fig. 1.

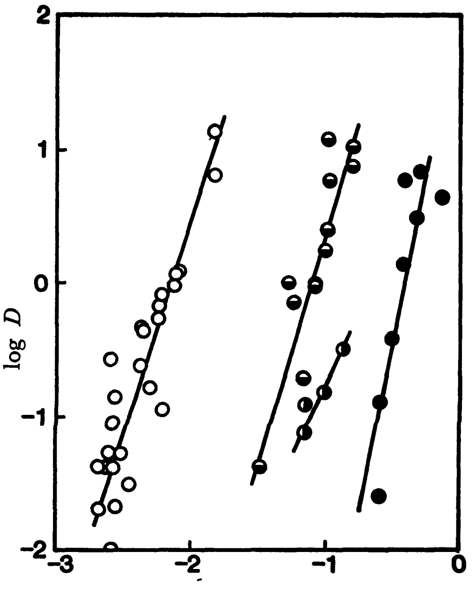

Fig. 3. Relation between log D for K(L)Pic and the water content of the solvent.
Symbols: see Fig. 1.

each solvent group, as is shown in Fig. 2. Such a linear relation holds for the extraction of KPic as well. The data points for the double-bond-containing and phenyl-substituted solvents show remarkable deviations; hence, these points are omitted from Fig. 2 so that the linear relationships for each solvent group can easily be seen.

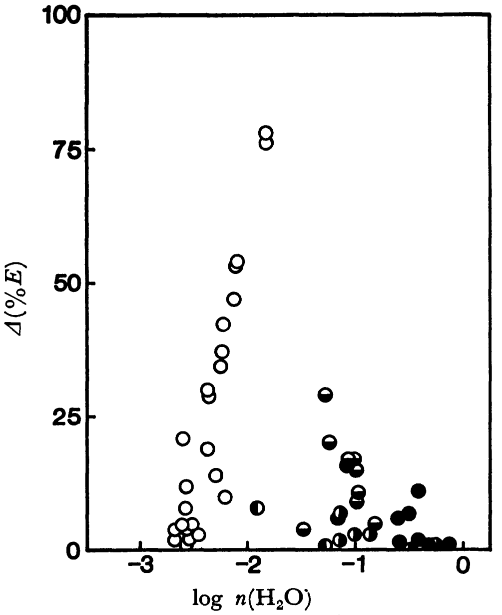

Fig. 4. Plot of $\Delta(\%E)$ *vs.* log $n(H_2O)$.
$\%E$=(picrate extracted/total picrate)×100. Symbols: see Fig. 1.

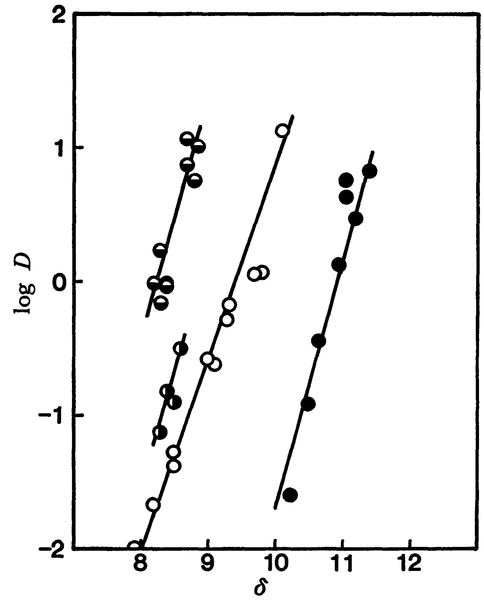

Fig. 5. Relation between log D for K(L)Pic and the solubility parameter of the solvent.
Symbols: see Fig. 1.

For the hydrocarbon solvents, the log D values for K(L)Pic also increase linearly with log s, though the fit is not so good as that which can be seen for the oxygen-containing solvents.

Water Miscibilities. Figure 3 shows that the log D values bear a linear relation to the logarithm of $n(H_2O)$, the mole fraction of water in the organic phase.

In order to investigate the effect of the complexation, percentage extraction increments, $\Delta(\%E)=\%E_{K(L)Pic}-\%E_{KPic}$, are plotted against log $n(H_2O)$ (Fig. 4). The extractability enhancement is maximal at $n(H_2O)=0.015$, indicating that the solvents which can dissolve water to a moderate extent are the best. The oxygen-containing solvents, contrary to the halogenated ones, exhibit a very slight enhancement. Taking into account the fact that crown-ether complexes are less stable in aqueous solutions than in alcohol solutions,[3] the reason for this is that the picrate complex is destabilized by the hydration of the potassium cations.

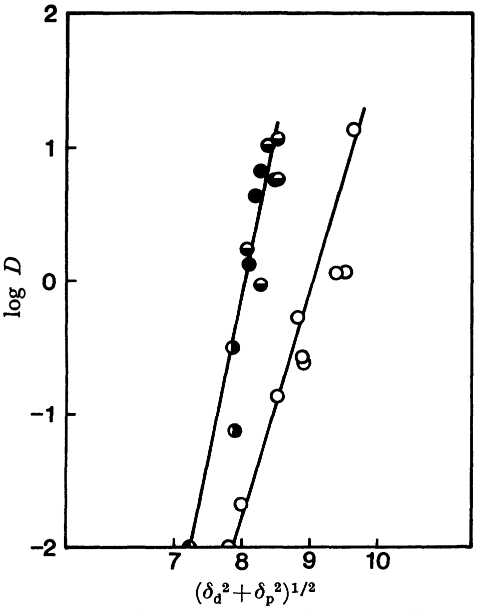

Fig. 6. Plot of log D for K(L)Pic *vs.* $(\delta_d^2+\delta_p^2)^{1/2}$. Symbols: see Fig. 1.

Solubility Parameters, δ. The regular solution theory has become increasingly important in chelate-extraction studies. However, little is known of its application to ion-pair extraction studies.

The dependence of the log D value for K(L)Pic on δ is illustrated in Fig. 5. The log D values increase linearly with δ. The slopes are identical for each solvent group except the halogenated one. It must be noted that modified δ values (*i.e.*, $\delta-1$ and $\delta-0.33$ for the phenyl-substituted and double-bond-containing solvents respectively) are used for the plot.

A solubility parameter can be divided into three components; thus, $\delta_0^2=\delta_d^2+\delta_p^2+\delta_h^2$, where δ_d, δ_p, and δ_h refer to the dispersion (London), polar (dipole-dipole), and hydrogen-bonding components of the solubility parameter respectively. A log D *vs.* $(\delta_d^2+\delta_p^2)^{1/2}$ plot yields a straight line for the oxygen-containing solvents, including strongly hydrogen-bonded solvents, such as alcohols, as is shown in Fig. 6; this finding indicates that the hydrogen-bonding components contribute much to the increase in δ_0 values, but little to the enhancement of the extractabilities. It must noted that data points for the hydrocarbon solvents fall of another regression line, though the reason for this is not clear.

Molar Volume, V. A linear relation is also found between log D and V, as is shown in Fig. 7. The molar volume looks promising as a measure of the extractability in the following respects: V bears a closer relation with log D, especially for the hydrocarbon solvents, and there is no need to use modified V values, not even for the

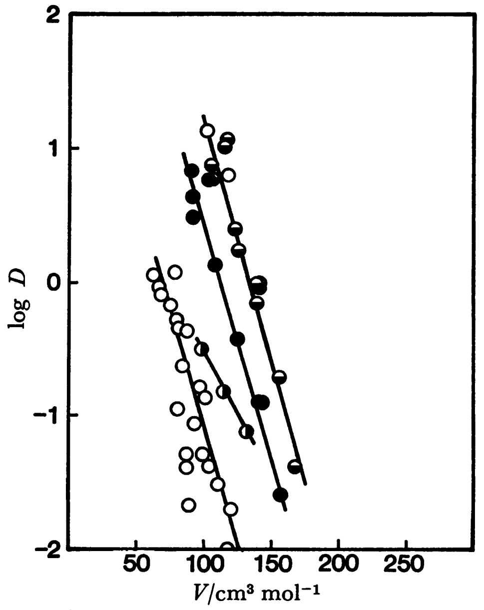

Fig. 7. Relation between log D for K(L)Pic and the molar volume of the solvent.
Symbols: see Fig. 1.

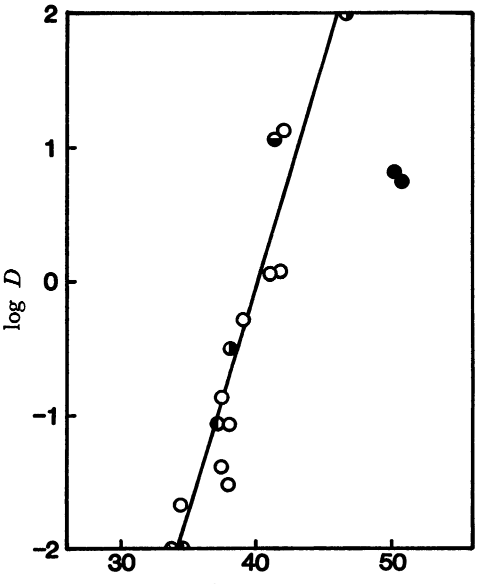

Fig. 8. Relation between log D for K(L) Pic and the E_T value of the solvent.
Symbols: see Fig. 1.

phenyl-substituted and double-bond-containing solvents. The data points for the chloro-substituted solvents (*i.e.*, CCl_4, $CBrCl_3$, *trans*-1,2-dichloroethylene, and 1,2-dichloroethane) and the nitro-substituted solvents show remarkable deviations from the regression line.

E_T Values. Several numerical scales for solvent polarity have been proposed based on the solvatochromism of indicators. The E_T values for 4-(2,4,6-triphenyl-1-pyridinio)-2,6-diphenylphenolate are known for as many as 70 solvents.[6] The dependence of log D on E_T is shown in Fig. 8. It is worth noting that the data points for all solvents except the alcohols fall on a linear line. A similar correlation is found to hold between log D and the spectral shift of 1-ethyl-4-(methoxycarbonyl)pyridinium iodide, which is known as Kosower's Z value,[7,8] though only 8 values are available. The data point for 1-butanol is significantly displaced from the regression line. The E_T values for Phenol Blue (N-[4-(dimethylamino)phenyl]-p-benzoquinone monoimine)[9] are found to correlate with log D, though the fit is not wholly satisfactory.

Miscellaneous. Kovats and Weisz have reported gas-chromatographic retention index values for 38 substances.[10] Although only 7 of them are available for the present purpose, they all fall on a line when plotted against log D.

On the other hand, no satisfactory correlation was observed between log D and Brownstein's S values.[11]

It can be concluded that, among the properties described here, the solubility parameters and Dimroth's E_T values are the most promising numerical scales for the extraction of the picrate.

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