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U.D.C. 543.241.5

The Differentiating Action of Oxygen-containing Solvents on the Strengths of Acids

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The present review examines the differentiating action of various oxygen-containing solvents on the strength of acids, chiefly carboxylic acids, and nitrophenols. The strength of the acids in these solvents is characterised by the dissociation constants (dielectric constant of solvent > 10) or by the conversion constants (dielectric constant of solvent < 10). The constants were determined by the buffer-free indicator method. The bibliography contains 143 references.

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I. INTRODUCTION

In the study of electrolytes in non-aqueous solvents, it is often found that the change in their strength is different from that observed in water. This effect of the solvents is called their "differentiating action".

The differentiating action of solvents on the strength of electrolytes, in particular acids, is an important problem in the general theory of solutions. This problem is also of considerable importance in the examination of the reactivities of substances and the mechanisms of reactions in solution. The ability of various non-aqueous solvents to

differentiate the strength of electrolytes is used successfully in chemical analysis. Non-aqueous titration has been finding increasing application in recent years, as indicated by the large number of papers devoted to this topic. These papers have been reviewed by Palit and coworkers[1] and by Kreshkov and coworkers[2-4].

A number of workers have studied the theory of the differentiating action of non-aqueous solvents on the strength of electrolytes. The concept of differentiating and levelling solvents was first introduced by Walden[5,6].

Considerable advances in the theory of electrolyte solutions and in particular the theory of the differentiating action of non-aqueous solvents on the strength of electrolytes have also been made by Soviet workers, particularly Izmailov and coworkers, who have continued the creative development of Mendeleev's ideas on the chemistry of dissolution and who have also introduced the achievements of the physical theory of solutions into the development of general ideas regarding solutions.

Previously, Brönsted[7,8], who studied the strength of acids in non-aqueous solutions, considered that the differentiating action of a solvent depends on its basic strength and dielectric constant. According to his theory, all acids with the same charge, even if of different character, show the same change in strength on going from one solvent to another.

Izmailov[9] showed that the strength of acids with the same charge but of different character (carboxylic acids and nitrophenols) change in different ways on going from water to various non-aqueous solvents. The magnitude of the relative change in the strength of the given acids characterises the differentiating action of the solvents.

According to Izmailov's quantitative theory of the influence of solvents on the strength of electrolytes[10-16], it is necessary, in the examination of the differentiating action of solvents on the strength of acids, to take account of the composition of the products of the reaction of the acid with the solvent, the dielectric constant (DC) and acid–base properties of the solvent, and the solvation of the anions of the acid by solvent molecules.

Hydroxyl-containing solvents may give reaction products with the 1 : 1 composition (with nitrophenols) or the 1 : 2 composition (with carboxylic acids). Solvents which do not contain hydroxyl can give reaction products with the 1 : 1 composition with both types of acid. The difference in the compositions of the products of the reactions of these solvents with acids of different character, compared with those for water, is responsible for their differentiating action. The differentiating action of solvents increases with decrease in the DC and with increase in the acidity of the solvents, and also with change in the energy of solvation of the anions of carboxylic acids.

An extensive review of papers on the differentiating action of non-aqueous solvents on the strength of electrolytes has been made by Izmailov[17,18]. Where necessary, we used material from this review in the examination of the differentiating action of oxygen-containing solvents on the strength of acids.

The present review examines chiefly oxygen-containing solvents of four classes: alcohols, ethers, ketones, and esters; the differentiating properties of acetic anhydride are also examined. The differentiating action of carboxylic acids as solvents was studied in detail by Izmailov and Shkodin[19-23]. They showed that the differentiating action of these solvents on the strength of acids depends chiefly on their DC. This class of solvent will not be examined in the present review.

II. DETERMINATION OF THE STRENGTH OF ACIDS IN SOLUTION

According to Izmailov's theory[10-16], the behaviour of acids in a solvent can be represented as follows:

$$HA + (m+n)M \rightleftarrows HAM_n + {}_mM \rightleftarrows MH_s^+ + A_s^- \rightleftarrows MH_s^+ \cdot A_s^- \quad (1)$$

The strength of an acid is characterised by the dissociation constant. Electrometric methods, however, measure only the value of K_{form}, which is equal to

$$K_{form} = \frac{[MH_s^+][A_s^-]\gamma^2}{[HA] + [HAM_n] + [MH_s^+ \cdot A_s^-]} . \quad (2)$$

The symbols in Eqn. (2) correspond to scheme (1); γ represents the mean activity coefficient of the ions.

In solvents with high DC, there are almost no associates, so that in these solvents the effective quantity K_{form} and the dissociation constant K_{diss} are equal:

$$K_{form} = K_{diss}\frac{[MH_s^+]^2\gamma^2}{C - [MH^+]\gamma}, \quad (3)$$

where C is the total concentration of acid. In solvents with high DC, electrometric, spectrophotometric, and indicator methods give the same values for the dissociation constants of acids.

In solvents with low DC, however, some of the ions are combined in ion pairs, and these cannot be detected by electrometric measurements. The formation of ion pairs is taken into account in spectrophotometric and indicator methods for determining the strength of acids, where they are regarded as free ions. This explains why in solvents with low DC the values of the dissociation constants of acids and bases determined by electrometric methods are smaller than the values of these constants found by spectrophotometric and indicator methods. This is illustrated in Table 1.

Table 1. pK values for acids in n-butanol.

Acids	pK, electrometric method (Refs.17 and 18)	pK, indicator method (Ref.24)
Acetic	10.35	9.22
Monochloroacetic	8.50	7.31
Dichloroacetic	7.30	6.09
Trichloroacetic	6.30	5.11
Benzoic	10.24	9.18
o-Nitrobenzoic	8.50	7.27
m-Nitrobenzoic	9.15	7.66
p-Nitrobenzoic	9.10	7.74
α-Dinitrophenol*	8.36	6.92
Picric	4.50	3.21

* Presumably 2,6-dinitrophenol, here and subsequently (Ed. of Translation).

The dissociation constants of acids determined by Izmailov using an electrometric method in 50% aqueous acetone are close to the values obtained using the indicator method[25], but in pure acetone[9,25] the two methods give different values. For all acids the dissociation constants determined by the electrometric method are slightly less than the constants obtained by the indicator method (see Table 2). A similar difference was observed by Izmailov and Gurevich[26] in the values of the dissociation constants of picric acid in butanol, found by electrometric and spectrophotometric methods.

In solvents with high dielectric constant, the dissociation constant of an acid is determined by the expression

$$K_{HA} = \frac{[H^+]^2\gamma^2}{(C-[H^+])\,\gamma_{HA}},$$

where γ is the mean activity coefficient of the ions of the acid. γ_{HA}, as the activity coefficient of a non-electrolyte, is close to unity. Since experimental measurements give not $[H^+]$ but $[H^+]\gamma$, and since for most non-aqueous solutions the values of γ are unknown, it is necessary to make the approximation of replacing $[H^+]$ by $[H^+]\gamma$ in the equation for the dissociation constant of the acid. This can be done for dilute solutions, in which γ does not differ greatly from unity. When these approximations are introduced, we obtain for the dissociation constant the expression

$$K_{HA} = \frac{[H^+]^2\gamma^2}{C-[H^+]\gamma}. \quad (4)$$

Table 2.

Acids	50% aqueous acetone		Acetone	
	pK, electrometric method (Ref.17)	pK, indicator method (Ref.25)	pK, electrometric method (Ref.17)	pK, indicator method (Ref.25)
Formic	5.23	5.06	—	9.57
Acetic	6.26	5.86	12.55	10.6
Monochloroacetic	4.28	4.41	9.80	9.21
Dichloroacetic	—	3.17	—	7.70
Trichloroacetic	2.20	2.19	—	6.51
Salicylic	4.18	4.39	9.53	9.08

For a basic indicator in a solution of an acid, we have the equilibrium

$$I_B + H_s^+ \rightleftarrows Ind\,H_s^+. \quad (5)$$

The constant for this equilibrium—the conversion constant of the indicator—is given by the relationship

$$K^I = \frac{[H^+]\gamma\,[I_B]}{[Ind\,H^+]\varkappa} \quad (6)$$

where I_B is the basic form of the indicator, $IndH^+$ the acid form of the indicator, and $\varkappa$ the activity coefficient of the ions of the indicator.

It follows from Eqn. (6) that $[H^+]\gamma = K_a^I$, where $a = \frac{[IndH^+]\varkappa}{[I_B]}$.

We then have

$$K_{HA} = \frac{(K^I a)}{C-K^I a}. \quad (7)$$

The value of K^I can be found[27-29] by solving Eqn. (7) for two acid concentrations C_1 and C_2, at which $a_1 = 1.2$ and $a_2 = 0.8$. It should be noted that the value of C determined colorimetrically is more accurate, the closer it is to unity. When the values of C_1 and C_2 are close to one another, it may be assumed that the mean activity coefficients of the ions of the acid are equal at these concentrations. In this instance we have for K^I the expression

$$K^I = \frac{a_1^3C_2 - a_2^3C_1}{a_1a_2(a_1-a_2)} = \frac{1.44C_2 - 0.64C_1}{0.384}. \quad (8)$$

The determination of K^I is carried out in dilute solutions of strong acids. The calculation of the dissociation constant of a monobasic acid in determinations with an indicator for which K^I has been found is carried out from Eqn.(7) for the acid concentration at which $a = 1$. The following relationship then yields the required constant K_{HA}:

$$K_{HA} = \frac{(K^I)^2}{C-K^I}. \quad (9)$$

If the acid being studied is much weaker than the acid $IndH_s^+$, $[H^+] \ll C$ in the equation for the dissociation constant. In this instance the dissociation constant is calculated using the equation

$$K_{HA} = \frac{(K^I)^2}{C}.$$

Most dissociation constants given by the data of the authors of the present review were obtained for the conditions indicated above. These conditions were achieved by choosing suitable indicators.

To determine the value of K_{HA} in media with low DC, use has been made[30] of the equation

$$K_{HA} = \frac{(K^I)^2 a}{C-K^I a}a^n, \quad (10)$$

where n is a coefficient which takes account of the association of the indicator and acid species. For $a = 1$, $a^n = 1$ for all values of n, so that the value of K_{HA} in this instance is also given by expression (9).

It is better to determine the values of a with a spectrophotometer than with a colorimeter, particularly for a two-colour indicator. When the basic form of the indicator exhibits appreciable absorption at the maximum of the spectroscopic curve of the acid form, it is suggested that a correction be introduced in the calculation[27,28] or that the method of Komar'[31] be used.

The determination of the dissociation constants of bases can be carried out analogously[32].

The method which we proposed for determining the conversion constants of indicators and the dissociation constants of acids and bases was verified for aqueous solutions[27,28]. The agreement in the values found with several acids indicates that the determination of the conversion constant of the indicator in a given solvent is correct. Table 3 gives as examples the values of the conversion constants of indicators obtained with various acids in ethylene glycol.

Several indicators are usually employed to determine reliably the dissociation constant of an acid in a given solvent. The values of pK for the dissociation of a given acid in a given solvent, obtained using different indicators and hence at different concentrations of the acid, differed in our determinations by not more than 0.2 pK unit. This is illustrated in Table 4. The reliability of the determination of dissociation constants by the indicator method which we proposed is also confirmed by the fact that the observed values of the constants differ little from the values measured using the spectrophotometric method (see Table 5).

The buffer-free indicator method for determining the dissociation constants of acids and bases has a number of advantages over other indicator methods. This method makes it possible to determine the dissociation constants of acids and bases and the conversion constants of indicators when none of these quantities are known.

The buffer-free indicator method in non-aqueous solutions should find wider application than the buffer method,

since many salts are sparingly soluble in non-aqueous solvents. Moreover, the ionic strength has a significant influence on the determination in non-aqueous solvents at ionic concentrations at which in water its influence could be neglected. It therefore becomes necessary to take account of the activity coefficients of the ions, but for most non-aqueous solvents these quantities are unknown. An advantage of the indicator method which we have proposed is that with slight approximation it becomes unnecessary to know the activity coefficients of the ions in a given solvent.

Table 3. Determination of the conversion constants of indicators with respect to various acids in ethylene glycol[33].

Acid	Indicator	
	Naphthyl Red	Quinoline Blue
Naphthalene-2-sulphonic	$3.50\cdot10^{-4}$	$2.30\cdot10^{-4}$
Dichloroacetic	$3.20\cdot10^{-4}$	—
Trichloroacetic	$3.80\cdot10^{-4}$	—
Picric	—	$2.43\cdot10^{-4}$

Table 4. Dissociation constants of acids in ethylene glycol[33].

Acids	K_{HA} relative to Quinoline Blue	K_{HA} relative to Naphthyl Orange	K_{HA} relative to Methyl Yellow	Mean K_{HA}	pK	ΔpK
Formic	$(2.42\pm0.38)\cdot10^{-5}$	—	—	$2.4\cdot10^{-5}$	4.62	0.87
Acetic	$(2.50\pm0.17)\cdot10^{-6}$	—	—	$2.5\cdot10^{-6}$	5.60	0.84
Monochloroacetic	$(7.97\pm1.12)\cdot10^{-5}$	$(6.65\pm0.01)\cdot10^{-5}$	—	$7.3\cdot10^{-5}$	4.14	1.27
Dichloroacetic	—	—	$(9.77\pm0.03)\cdot10^{-4}$	$9.8\cdot10^{-5}$	3.01	1.71
Benzoic	$(6.40\pm0.04)\cdot10^{-6}$	—	—	$6.4\cdot10^{-6}$	5.19	0.99
p-Nitrobenzoic	$1.98\cdot10^{-5}$	—	—	$2.0\cdot10^{-5}$	4.70	1.28
m-Nitrobenzoic	$1.85\cdot10^{-5}$	—	—	$1.9\cdot10^{-5}$	4.72	1.28
Salicylic	$(8.47\pm0.9)\cdot10^{-5}$	$(5.50\pm0.66)\cdot10^{-5}$	—	$7.0\cdot10^{-5}$	4.15	1.18
α-Dinitrophenol	$(5.33\pm0.38)\cdot10^{-5}$	—	—	$5.3\cdot10^{-5}$	4.28	0.16
β-Dinitrophenol*	$(5.01\pm0.3)\cdot10^{-5}$	—	—	$5.0\cdot10^{-5}$	4.30	0.53
Boric	$(2.74\pm0.06)\cdot10^{-6}$	—	—	$2.7\cdot10^{-6}$	5.57	−3.69

Note. ΔpK is the difference between the pK values found for the given acid in the solvent used and in water.

* Presumably 3,5-dinitrophenol, here and subsequently (Ed. of Translation).

Table 5. pK values for picric acid.

Alcohol	Spectrophotometric method	Indicator method
t-Butyl[34]	4.43	4.75
n-Hexyl[34]	4.23	4.36
n-Butyl[24]	3.26*	3.21

* Value obtained by Izmailov and Gurevich[26].

It should be noted that the graphical method usually employed to determine the conversion constants of indicators and the dissociation constants of acids or bases is difficult in solvents with low DC, since the regular features of the change in the ratio $[IndH^+]/[Ind]$ with change in acid concentration is complicated by the phenomena of ion association. In solvents with low dielectric constant the strength of acids is characterised by the equilibrium constant for the formation of ion pairs from molecules of the acid:

$$HA \rightleftarrows H_s^+A_s^- . \qquad (11)$$

Following Izmailov, the constant K_{tr} for equilibrium (11) is called the transformation constant (see scheme 1). These equilibrium constants for acids were determined by Kolthoff and Bruckenstein[35], using the indicator method. They examined the following equilibrium between acid and indicator:

$$I_B + HA \rightleftarrows IH_s^+ \cdot A_s^- . \qquad (12)$$

This equilibrium is established in an indifferent solvent, but in a non-indifferent solvent the following equilibrium is energetically more probable:

$$I_B + H_s^+ \cdot A_s^- \leftrightarrows IH_s^+ \cdot A_s^- . \qquad (13)$$

It is evident that the constant for equilibrium (12) depends on the strength of the acid. We proposed a method[29,36] for determining the strength of an acid using the constant for equilibrium (13), that is, the transformation constant of the indicator K_{tr}^I, which is independent of the strength of the acid with which the determination is carried out.

Solvents whose DC are low, but not too low, contain both free ions and ion pairs. For the separate determination of these species, and hence the determination of the constants K_{diss} and K_{tr}, it is necessary to use both electrometric and spectrophotometric or indicator methods. In non-aqueous solvents, particularly those with low DC, the electrometric measurements are often difficult, and comparatively few data are available for these solvents. Difficulties are also encountered in the spectrophotometric determinations, due to the fact that the absorption maxima of the acids or their ions and the solvent are close together, or due to photolysis.

The data obtained by the authors of the present review on the determination of the strength of acids by the indicator method are conditional. Since methods were not available for the separate measurement of the concentrations of free ions and ion pairs, conditional values of the dissociation constants were calculated from the data obtained in solvents with DC > 10, and for solvents with DC < 10 the overall effect was related to the conditional value of the transformation constant of the acid.

1. Alcohols and Ethers

Data on the strength of acids in various alcohols have been obtained by a variety of methods[17,18,37-46]. In an analysis of published data on the strength of acids in methanol, ethanol, and n-butanol, obtained from electrometric measurements, Izmailov[17,18] concluded that alcohols produce a marked decrease in the dissociation constants of all acids, but that the decrease in strength in alcohols compared with water is not quite the same for carboxylic acids and nitrophenols. Izmailov noted that the specific influence of alcohols on the strength of acids is shown more clearly in n-butanol. Thus alcohols differentiate the strength of acids to a slight extent, although they are typical levelling solvents with respect to salts[5,6,47]. The slight increase in the differentiating action of alcohols on the strength of acids in the series methanol (DC = 31.5), ethanol (DC = 24.0), and n-butanol (DC = 17.0) was attributed to the decrease in the DC of the alcohols in this series.

Table 6. pK values for acids in hydroxyl-containing solvents.

Acids	DC	Solvents: water [17,18]	n-butanol [24]	n-pentanol [53]	n-hexanol [34]	n-heptanol [53]	n-octanol [53]	n-decanol [53]	isobutyl alcohol [24]	isopentyl alcohol [48]	t-butyl alcohol [34]	cyclohexanol [50]	benzyl alcohol [49]	phenol [52]	ethylene glycol [33]	2-chloroethanol [33]	diethylene glycol [51]	diacetone alcohol [51]
			17.1	13.9	13.3	12.0	10.34	—	17.7	15.5	10.9	15.0	13.1	9.78	37,70	25.80	31.7	18.2
	°C	25	20±2	20±2	20±2	20±2	20±2	20±2	20±2	20±2	27±2	27±2	20±2	50±2	20±2	20±2	20±2	20±2
Formic		3.75	8.03	—	7.92	—	—	—	8.85	8.92	8.82	9.02	8.34	5.17	4.62	—	6.64	—
Acetic		4.75	9.22	—	9.26	—	—	—	10.35	10.51	10.30	10.68	9.71	6.58	5.60	7.72	7.35	—
Monochloroacetic		2.86	7.31	7.85	7.24	6.35	—	—	8.11	8.48	8.51	8.60	7.88	4.85	4.14	5.55	5.82	—
Dichloroacetic		1.30	6.09	6.46	6.29	5.76	7.48	3.34*	6.85	7.07	7.20	7.19	6.43	—	3.01	—	4.38	7.60
Trichloroacetic		0.70	5.11	5.47	5.51	4.88	6.53	2.62*	5.62	5.32	6.82	6.04	5.37	—	—	—	2.82	6.39
Benzoic		4.20	9.18	9.53	9.11	8.40	—	—	10.20	10.92	9.80	11.34	9.62	6.80	5.19	7.68	6.96	—
o-Nitrobenzoic		2.17	7.27	8.17	7.22	6.90	8.77	—	8.37	—	8.57	8.70	—	4,75	—	—	—	—
m-Nitrobenzoic		3.49	7.66	8.53	7.85	7.16	9.77	—	—	9.17	9.20	9.40	8.60	6.15	4.72	6.43	5.64	—
p-Nitrobenzoic		3.40	7.74	—	7.52	—	—	—	8.78	9.07	9.44	9.58	8.38	5.70	4.70	6.49	6.24	—
Salicylic		2.97	7.51	8.14	7.48	6.71	9.33	—	8.25	8.50	8.66	8.78	8.40	5.30	4.15	5.42	5.82	—
α-Dinitrophenol		4.02	6.92	7.49	6.89	6.11	8.74	—	7.54	7.89	7.30	7.58	8.34	7.04	4.28	6.15	5.48	8.43
β-Dinitrophenol		3.80	6.92	7.24	6.85	5.90	8.23	—	7.54	7.82	6.89	8.10	8,38	6.62	4.28	6.25	5.48	8.43
Picric		0.80	3.21	3.92	4.36	3.70	4.29	1.21*	3.96	4.30	4.70	3.57	4.42	—	—	—	3.12	—
Boric		9.24**	—	—	—	—	—	—	—	—	—	—	—	—	5.57	—	—	—

* pK_{tr}. ** pK_1.

Table 7. $\Delta pK = pK_{\text{in alcohol}} - pK_{\text{in water}}$.

Acids	Solvents: n-butanol	n-pentanol	n-hexanol	n-heptanol	n-octanol	isobutyl alcohol	isopentyl alcohol	t-butyl alcohol	cyclohexanol	benzyl alcohol	phenol	ethylene glycol	2-chloroethanol	diethylene glycol	diacetone alcohol
Formic	4.28	—	4.17	—	5.83	5.10	5.17	5.07	5.27	4.59	1.42	0.87	—	2.89	—
Acetic	4.47	—	4.50	—	—	5.59	5.75	—	5.92	4.95	1.82	0.84	2.96	2.59	—
Monochloroacetic	4.45	4.98	4.37	3.49	—	5.24	5.61	5.64	5.73	5.01	2.00	1.27	2.68	2.95	—
Dichloroacetic	4.79	5.16	4.99	4.46	6.18	5.55	5.77	5.90	5.98	5.13	—	1.71	—	3.08	6.30
Trichloroacetic	4.41	4.77	4.81	4.18	5.83	4.92	4.62	6.12	5.34	4.67	—	—	—	2.12	5.69
Benzoic	4.98	5.33	4.91	4.20	—	6.00	6.72	5.60	7.14	5.42	2.60	0.99	3.48	2.76	—
o-Nitrobenzoic	5.10	5.97	5.02	4.73	6.60	6.20	—	6.37	6.50	—	2.20	—	—	—	—
m-Nitrobenzoic	4.17	5.06	4.36	4.67	6.28	—	5.68	5.71	5.91	5.11	2.68	1.28	2.96	2.15	—
p-Nitrobenzoic	4.32	—	4.12	—	—	5.38	5.67	6.04	6.17	4.96	2.30	1.28	3.07	2.84	—
Salicylic	4.54	5.17	4.51	3.74	6.36	5.28	5.53	5.69	5.80	5.12	2.32	1.18	2.45	2.85	—
α-Dinitrophenol	2.90	3.47	2.87	2.09	4.72	3.52	3.87	3.28	3.55	4.32	2.94	0.16	2.13	1.46	4.41
β-Dinitrophenol	3.12	3.44	3.05	2.10	4.43	3.74	4.02	3.09	4.30	4.58	2.85	0.53	2.41	1.68	4.63
Picric	2.41	3.12	3.56	2.90	3.49	3.16	3.50	3.90	2.77	3.62	—	—	—	—	—
Boric	—	—	—	—	—	—	—	—	—	—	—	3.67	—	—	—

We used the buffer-free indicator method to study the strengths of a series of acids of different character in various primary, iso-, secondary, and tertiary alcohols, and also in alcohols with two functional groups: ethylene glycol, 2-chloroethanol, diethylene glycol, and diacetone alcohol [24,33,34,48-53]. In alcohols with intermediate DC values, the dissociation constants of the acids were calculated, and in alcohols with DC less than 10, the transformation constants were calculated. The results are given in Table 6, which also gives the pK values for the acids in water [17,18]. The decrease in the strengths of carboxylic acids in alcohols relative to their strengths in water is different for different acids; the strengths of nitrophenols change to a smaller extent.

The change in the strength of acids on going from water to a non-aqueous solvent is characterised by the quantity $\Delta pK = pK_{\text{in alcohol}} - pK_{\text{in water}}$. The greater the quantity ΔpK, the greater the decrease in the strength of acids in the given solvent compared with water. The values of ΔpK obtained for the alcohols studied are given in Table 7. The decrease in the strength of *o*-nitrobenzoic acid on going from water to alcohols is greater than the decrease in strength shown by all other carboxylic acids. This phenomenon can be explained on the basis of the steric effects arising in the reaction of the molecules and ions of this acid with the solvent. In the *o*-nitrobenzoic acid molecule, an intramolecular hydrogen bond may be formed between the NO_2 and COOH groups, and this is broken on interaction with the solvent. Thus the reaction of the molecules of this acid with the solvent depends on steric effects to a greater extent than the reaction of other carboxylic acids whose molecules do not contain an intramolecular hydrogen bond. For salicylic acid, whose molecule contains a hydroxyl group in the *ortho*-position, an effect similar to that observed for *o*-nitrobenzoic acid should have been found. However, the decrease in the strength of this acid on going from water to alcohols was found to be approximately the same as that for other carboxylic acids. As noted above, the strength of an acid depends on the reaction of the acid with the solvent and on the subsequent solvation of the ions formed. Thus the observed contradictions are apparently explained by the suggestion [54-57] that the salicylate ion formed on ionisation of the acid contains an intramolecular hydrogen bond and is stable.

The decrease in the strength of nitrophenols on going from water to alcohols with two functional groups is slightly smaller than that observed for carboxylic acids, but the

decrease in strengths is almost the same in diethylene glycol.

It is convenient to estimate the differentiating action of solvents from graphs giving the dependence of pK for the acids in alcohol on their pK values in water. As already noted[17], different straight lines are obtained graphically for acids of different character (carboxylic acids and nitrophenols) in differentiating solvents. For some acids, particularly *o*-nitrobenzoic acid, the pK values do not lie directly on the straight line for carboxylic acids, because of the specific interaction of the acid with the solvent. The differentiating properties of a given solvent can be estimated from the distance between the straight lines on the graph of the dependence of pK for the acids in the non-aqueous solvent on the pK values for the acids in water. This distance (Δ'pK), expressed in pK units, gives the difference between the change in the strength for acids of different chemical character on going from water to the non-aqueous solvent expressed in orders of magnitude. The Δ'pK values obtained from data on the strength of acids in alcohols (Table 6) are given in Table 8.

Table 8. Differentiating action of alcohols.

Alcohols	DC	Δ'pK (from graphs)	Alcohols	DC	Δ'pK (from graphs)
Benzyl	13.1	1.0	Isopentyl	15.5	1.9
n-Butyl	17.1	1.8	t-Butyl	10.9	2.4
n-Pentyl	13.9	1.9	Phenol	10	−0.8*
n-Hexyl	13.3	1.5	Cyclohexanol	15.0	2.5
n-Heptyl	12.0	1.7	Ethylene glycol	37.70	≈1.0
n-Octyl	10.34	2.0	Diethylene glycol	31.69	1.1
n-Decyl	<10	1.6*	2-Chloroethanol	25.8	0.8
t-Butyl	17.7	1.9	Diacetone	18.2	1.6*

* Estimated approximately from the data in Table 6.

On going from n-butanol to n-octanol in the series of normal alcohols, the differentiating properties change little, although the DC values of the alcohols decrease. Thus the differentiating properties of these alcohols cannot be attributed to the influence of their DC.

The differentiating properties of alcohols are influenced by their acid–base properties. The acidity of simple aliphatic alcohols decreases with increase in the electron-donating properties of the alkyl group[58]. Work by Gerrard and Macklen[59-61] on the solubility of hydrogen chloride in alcohols showed, however, that n-butanol, n-hexanol, n-heptanol, and n-octanol have almost identical electron-donating properties. Thus for the example of these normal alcohols it is possible to follow the influence of one predominant factor—the increase in the length of the alkyl radical of the alcohol—on the differentiating properties of the alcohol.

It can be seen from the results obtained that the increase in the length of the alcohol radical from butanol to decanol has little influence on the differentiating properties of the alcohol, since the increase in the radical of the primary alcohol hardly affects the screening of the functional group of the alcohol and does not produce any significant steric effects in the reaction of the molecules of these solvents with carboxylic acid dimers.

Comparison of the differentiating properties of the normal alcohols and iso-alcohols leads to the conclusion that branching of the radical in the alcohol molecule at a carbon atom which is not joined to a hydroxyl group produces little change in the differentiating properties of the alcohols.

Of the alcohols with one functional group which we studied, benzyl alcohol shows the weakest differentiating properties. The DC of this alcohol is almost the same as that of n-hexanol. The weak differentiating properties of benzyl alcohol can probably be attributed to the fact that it exhibits stronger acidic properties than the other normal alcohols, and its radical has little steric effect on the reaction of two molecules of the alcohol with a molecule of the carboxylic acid. Thus carboxylic acids are stronger acids in benzyl alcohol than in other alcohols.

The more acidic solvent, phenol, with a planar radical, produces a change in the relative strength of acids which is the opposite of that observed for alcohols, in spite of the fact that phenol has a low DC. The decrease in the strength of carboxylic acids in phenol is less than that shown by nitrophenols.

The secondary alcohol cyclohexanol is a differentiating solvent, although its DC is of the same order of magnitude as the DC of normal alcohols, iso-alcohols, and benzyl alcohol. It is also a more basic solvent than the alcohols already considered. Thus the marked differentiating action of this alcohol on the strength of acids is apparently related to the spatial complexity of its radical.

t-Butyl alcohol is also a strongly differentiating solvent.

It may be concluded that the differentiating properties of secondary and tertiary alcohols are related to the spatial complexity of the radicals of these alcohols close to their functional groups; this creates considerable steric hindrance in the reaction of the molecules of these alcohols with carboxylic acid dimers.

Of the alcohols studied, ethylene glycol has the highest DC, so that it should exhibit weaker differentiating properties than the other alcohols. The data obtained, however, indicate that ethylene glycol is a slightly stronger differentiating solvent than benzyl alcohol and 2-chloroethanol—solvents with smaller DC.

Published data[58-70] show that all the alcohols studied differ little in acid–base properties, with the exception of ethylene glycol and 2-chloroethanol.

2-Chloroethanol is the most strongly acidic of the alcohols studied, so that despite the fact that its radical is more complex than the radical of benzyl alcohol, it exhibits weaker differentiating properties.

Although ethylene glycol has a high DC and is a more acidic solvent than benzyl alcohol, its differentiating action on the strength of acids is approximately the same, so that its radical produces greater steric hindrance in the reaction with carboxylic acid dimers than benzyl alcohol. The strength of boric acid has been determined in ethylene glycol; boric acid reacts with this solvent to form a complex which behaves as a monobasic acid[71].

Diethylene glycol is $\beta\beta'$-dihydroxydiethyl ether. The presence of the ether group explains why it is a stronger base than ethylene glycol. The oxygen of this ether group can react with acids. This atom is screened to a greater extent, however, than the oxygen of the hydroxyl group, so that the differentiating properties of diethylene glycol are stronger than those of ethylene glycol.

From its DC, the differentiating properties of diacetone alcohol should be the same as those of isobutyl alcohol, but on the basis of the structure of its radical it should exhibit stronger differentiating properties than all other alcohols. According to the studies of Badger and Bauer[72,73], diacetone alcohol contains an intramolecular hydrogen bond. These authors also compare the structure of this alcohol

with that of t-pentyl alcohol. Thus the molecule of this alcohol should create greater steric hindrance in its reactions not only with carboxylic acids but also with nitrophenols. As a result, the change in the relative strength of acids of different character is approximately the same in this solvent as in isobutyl alcohol.

As noted above, one of the factors influencing the differentiating properties of solvents is the difference in the solvation of the anions of acids of different character by these solvents. Izmailov and coworkers[74-78] showed that on going from water to levelling solvents the change in the solvation energy of the molecules becomes greater than the change in the solvation energy of the ions; in differentiating solvents, however, the opposite relationship is observed. Thus in the examination of the differentiating properties of solvents it is necessary to take into account the reaction of both the ions and the molecules of the acid with the molecules of the solvent.

To obtain information on the relative change in the energy of solvation of the anions of carboxylic acids and nitrophenols in the alcohols studied, we determined the heats of dissolution of the diethylammonium salts of carboxylic acids and nitrophenols[79-81]. The heats of solvation of the ions in different solvents are fairly close, but, as shown by Izmailov[82], even slight differences in the values lead to a marked change in the strength of the acid.

Table 9. Heats of dissolution ΔH, kcal mole^{-1}, of diethylammonium salts in alcohols and cyclohexane[79-81].

Diethylammonium salt	Water (27°C)	Water (41°C)	2-Chloroethanol (27°C)	Benzyl alcohol (27°C)	Ethylene glycol (27°C)	Diethylene glycol (27°C)	Cyclohexanol (41°C)	t-Butyl alcohol (27°C)	Cyclohexanol (27°C)
Chloride	0.3	2.6	—2.0	0.7	2.1	2.1	4.0	—	0.2
Bromide	1.8	3.8	0.7	1.9	3.5	2.0	2.4	—	5.6
Trichloroacetate	1.8	5.3	1.7	2.2	3.6	3.0	8.6	7.5	5.6
Salicylate	2.8	5.9	—0.8	2.6	3.8	1.4	5.2	4.5	4.5
Benzoate	*	0.8	—1.4	2.2	2.9	*	4.6	8.1	5.2
Acetate	—0.8	—4.9	1.1	2.7	3.6	3.3	—	—	8.7
α-Dinitrophenolate	—4.1	10.5	2.9	4.4	5.4	—	10.9	—	5.7
β-Dinitrophenolate	4.6	8.7	3.5	4.9	6.0	—	8.2	—	5.4
Picrate	4.7	8.0	3.0	2.9	5.1	*	7.7	9.1	3.5

* Sparingly soluble salt.

In the analysis of the data in Table 9 it is necessary to take into account the familiar ideas of physical chemistry, according to which an increase in the exothermicity of the dissolution of a given salt in different solvents is due to an increase in the energy of solvation of its ions.

The data in Table 9 indicate that the relative exothermic nature of the solvation of the anions of acids increases in the order: t-butyl alcohol, ethylene glycol, diethylene glycol, benzyl alcohol, 2-chloroethanol. The most strongly exothermic process is the solvation of the salts in 2-chloroethanol, and this is evidently related to the fact that the acidic properties of this alcohol are stronger than those of the other alcohols. With increase in the acidity of the alcohol, the hydrogen bond which it forms with the ions of the acids studied disappears.

It can be seen from the heats of dissolution of the salts (Table 9) that the exothermic nature of the solvation of the anions of the acids decreases considerably on going from water to cyclohexanol (with the exception of salicylate). For the salts formed by nitrophenols, the changes in the heats of solvation are not large. Thus the differentiating properties of cyclohexanol are related to the fact that the heats of solvation of the anions of carboxylic acids are smaller in cyclohexanol than in water.

The heats of solvation of the salicylate ion in different alcohols are approximately the same (judging from the heats of dissolution of diethylammonium salicylate, given in Table 9). This can be attributed to the fact that the salicylate ion contains an intramolecular hydrogen bond, so that it reacts weakly with the OH group of the solvent and the spatial complexity of the radical of the solvent has no significant influence on the heat of solvation of this ion.

As already noted, in the examination of the differentiating properties of solvents it is necessary to take into account the reaction of not only the ions but also the molecules of the acid with the molecules of the solvent. Izmailov showed that the energy of solvation of the molecules of acids depends on the strength of the complex formed between the acid and the solvent. If the solvent is more basic, the energy of solvation of the molecules will be greater, and the solvation will become more exothermic. On the basis of the data which we obtained[79] (Table 10) it may be concluded that the change in the integral heats of dissolution of benzoic and salicylic acids and α-dinitrophenol on going from the levelling solvent benzyl alcohol to the differentiating solvent cyclohexanone (a ketone) is not large. The energy of the reaction of the molecules of the acids with cyclohexanone is greater than that for benzyl alcohol, since cyclohexanone is a slightly more basic solvent than benzyl alcohol.

Table 10. Integral heats of dissolution of acids[79] (27°C).

Acids	ΔH, kcal mole^{-1}	
	cyclohexanone	benzyl alcohol
Benzoic	3.5	4.7
Salicylic	2.1	3.8
α-Dinitrophenol	3.9	5.3

It may therefore be concluded that the differences in the differentiating properties of alcohols are related chiefly to differences in the energies and heats of solvation of the anions of carboxylic acids compared with the anions formed by nitrophenols. The increase in the differentiating action of the solvents is related to the decrease in the exothermic nature of the solvation of the ions of the carboxylic acids. The exothermic nature of the solvation of the anions of carboxylic acids in turn decreases with increase in the spatial complexity of the radicals of the alcohols.

It follows from the foregoing that the differentiating action of alcohols on the strength of acids is due to a number of factors: the spatial complexity of the radicals of the solvent, the difference in the solvation of the anions of acids of different character (this also depends on the spatial complexity of the solvent molecules), and the acidity of the solvent. Both levelling and differentiating solvents can be found among alcohols, depending on the combination of these factors.

Like alcohols, ethers contain an alkoxy-oxygen, which is screened by two radicals. Thus the reaction of ethers

with acids should be influenced considerably by steric factors associated with the screening of the functional group of the ether by the radicals. This is indicated by published data[83-86] on the basis of which we should expect that the differentiating properties of ethers will also depend to a marked extent on the nature and spatial complexity of their radicals.

We studied the strength of various carboxylic acids and nitrophenols in various ethers: diphenyl (diphenyl oxide), methyl phenyl (anisole), diethyl, dibenzyl, di-(2-chloroethyl) (Chlorex), dibutyl, and di-isopentyl[36,87,88]. All these ethers, with the exception of Chlorex, have low dielectric constants (in the range 2–5), so that the strength of acids in these solvents should be characterised by the transformation constants, which we determined by the proposed method. The transformation constants of picric acid were first determined spectrophotometrically. We recorded the spectra of solutions of picric acid in the ethers and with the addition of a strong base in the range 370–470 nm. The spectra of solutions of picric acid in a given ether with the addition of an excess of diethylamine or piperidine coincided. The spectroscopic curves for the picrate solutions show a slight maximum in the range 400–420 nm, characteristic of the associated ions of picric acid[89]. We calculated the values of the transformation constants for picric acid in ethers from the absorption at various wavelengths in the spectral range studied. It was found that the calculated values of the constants remained almost constant in the wavelength range 440–480 nm. With decrease in wavelength, however, the values of the constants gradually increased. This is apparently due to the fact that in this range, absorption by molecules of the acid increases gradually towards shorter wavelengths, and this was not taken into account in the calculation. Table 11 therefore gives the mean values of pK_{tr} for picric acid, calculated for the wavelength range 440–480 nm. The calculation of the transformation constants of picric acid was based on the assumption that the ionic associates obtained by the reaction of picric acid with strong bases (diethylamine or piperidine) and with ethers acting as bases have the same absorption spectra in the range used for the calculations; molecules of picric acid do not absorb in this range. Justification for this assumption is provided by the agreement observed in the dissociation constants of picric acid in alcohols, determined by spectrophotometric and indicator methods. The spectrophotometric determination of the dissociation constants of this acid was based on the same assumptions as the determination of its transformation constants in the ethers. The transformation constants of the indicators were then determined with respect to picric acid, and the values were used to determine the transformation constants of carboxylic acids and dinitrophenols.

Examination of the pK_{tr} values for the acids in the ethers studied (Table 11) shows that the strengths of nitrophenols in the ethers studied do not differ greatly. The strengths of carboxylic acids in ethers with different radicals, however, differ sharply and a correlation is not observed between the basic strength of the ethers and the strengths of carboxylic acids in these ethers.

According to published data[61,90-95], the ethers studied can be arranged in the following order of increasing basic strength: diphenyl oxide < anisole < Chlorex < dibenzyl ether < diethyl ether < dibutyl ether.

In diphenyl oxide—the ether with the lowest basic strength—the carboxylic acids are much weaker than in the more basic diethyl ether, and the value of K_{tr} for trichloroacetic acid is smaller by almost three orders of magnitude in dibutyl ether than in diphenyl oxide. The strength of the carboxylic acids decreases with increase in the spatial complexity of the radicals of the ether (Table 11). The differentiating action of ethers is characterised by the values of $\Delta' pK_{tr}$, found from graphs giving the dependence of the values of pK_{tr} in the corresponding ether on the pK values in water (Table 12).

Table 11. pK_{tr} values for acids in ethers[36,87,88].

Acids		Solvents					
		dibutyl ether	diethyl ether	benzyl ether	anisole	diphenyl oxide	Chlorex
	DC	3.06	4.34	5.1	4.33	2.35	21.20
	°C	20±2	20±2	20±2	20±2	30±2	20±2
Formic		—	—	5.05	4.74	4.04	—
Acetic		—	—	—	4.85	5.48	—
Monochloroacetic		—	5.85	4.54	3.97	3.05	—
Dichloroacetic		—	4.52	2.54	2.00	1.82	7.47*
Trichloroacetic		3.07	2.52	2.26	1.00	0.35	6.62*
Benzoic		—	—	—	5.71	5.23	—
Salicylic		—	5.76	—	4.05	3.41	—
o-Nitrobenzoic		—	5.12	—	3.67	2.65	—
m-Nitrobenzoic		—	—	—	4.42	3.65	—
p-Nitrobenzoic		—	—	—	4.62	4.08	—
α-Dinitrophenol		—	4.87	—	4.24	5.00	—
β-Dinitrophenol		—	4.23	5.20	4.38	4.14	—
Picric		1.09	1.52	2.00	1.05	1.57	5.52*

* pK.

Table 12.

Ethers	$\Delta' pK_{tr}$
Diphenyl oxide	0
Anisole	0.3
Dibenzyl	0.2
Diethyl	1.5
Dibutyl	2.0
Chlorex	1.2*

* $\Delta' pK$.

Examination of the results obtained shows that diphenyl oxide is a levelling solvent and that in this solvent we even observe a slight relative decrease in the strength of nitrophenols compared with carboxylic acids. We observed a similar but more clearly defined influence on the strength of acids in phenol. Anisole and dibenzyl ether show a very slight differentiating action, whereas ethers with saturated radicals are strongly differentiating solvents, and this property becomes more marked with increase in the size of the radicals. Diethylammonium and piperidinium picrates are insoluble in isopentyl ether, so that only the concentrations of picric and trichloroacetic acids at which half of the indicator Naphthyl Red is converted into the acid form were determined. These data[88] show that the differentiating properties of di-isopentyl ether are similar to those of dibutyl ether, that is, di-isopentyl ether is a strongly differentiating solvent. For Chlorex, $\Delta' pK$ = 1.2, and this characterises it as a differentiating solvent, although its differentiating properties are weaker than those of the other ethers having saturated radicals studied.

Ethers are solvents which cannot act as proton donors, so that it might be expected that they would all be differentiating solvents. The observed variation between their differentiating properties, which depend on the structure of the radicals in the ether molecule, indicates that steric factors have a marked influence on the reaction of the carboxylic acid dimers with the molecules of the ether.

To investigate the factors influencing the differentiating properties of ethers, we studied the heats of dissolution of benzoic acid and two dinitrophenols, and also diethylammonium β-dinitrophenolate, benzoate, and trichloroacetate in anisole, Chlorex, and dibutyl ether. The results[88] indicate that the relative change in the heats of dissolution of the acids and their salts on going from a levelling ether to a differentiating ether is not large, and its nature is such that it cannot explain the variation in the differentiating properties of ethers.

Information on the mechanism of the reaction of carboxylic acids with alcohols can be obtained from the infrared spectra of solutions of these acids in the alcohols.

Izmailov and coworkers[89,96,97] previously studied the reaction of carboxylic acids with alcohols from the Raman spectra in the range of the ν_{max} band of the C=O group. Only the reaction of carboxylic acids with weakly differentiating alcohols was studied.

Carboxylic acids exist in the form of dimers. The monomeric form of the acid is produced in solution as a result of the reaction of the acid dimers with solvent molecules. In the acid dimer, the hydrogen bond between the hydroxyl group of the acid and the carbonyl oxygen is stronger than that between this oxygen and the hydroxyl group of the alcohol which reacts with the acid, because the hydroxyl group of the acid has a greater tendency to give up a proton than the hydroxyl group of the alcohol. Thus breakdown of the dimer should take place as a result of the reaction of the oxygen of the hydroxyl group of the alcohol with the hydrogen of the hydroxyl group of the acid. To determine how carboxylic acids react with levelling and differentiating alcohols, we studied the infrared spectra of trichloroacetic acid in various alcohols, examining the region of the stretching vibrations of the C=O and OH (OD) groups of the acid[98].

No significant displacement of the main ν_{max} band due to the C=O group was observed on going from one alcohol to another. This indicates that the alcohols which we studied influence the position of the band due to the carbonyl group of the acid in the same way.

We assigned the main intense band (~ 1750 cm^{-1}) to the vibrations of the C=O group of the acid monomers, since it may be assumed that the carboxylic acid dimers are broken down in solvents capable of forming a strong hydrogen bond with the acid molecule. In this connection it may be noted that according to data obtained by Izmailov and coworkers[89,97] and ourselves[98], the νC=O band of the acid dimers in the infrared and Raman spectra was observed only in fairly concentrated solutions of acetic acid in alcohols.

In the infrared spectra of solutions of trichloroacetic acid in strongly differentiating solvents (cyclohexanol and t-butyl alcohol) we observed a weak band in the range 1700–1715 cm^{-1}, which may be assigned to the vibrations of the C=O group of the acid dimer. On dilution, the intensity of this band decreased, and the intensity of the band due to the C=O group of the acid monomers increased. In the spectra of solutions of trichloroacetic acid in weakly differentiating alcohols, we did not observe the band due to the C=O group of the acid dimers. It can evidently be assumed that the given solvents react more strongly with trichloroacetic acid than do differentiating solvents. Thus the quantity of dimers in these solvents is not large and has no influence on the stretching vibrational band of the carbonyl group of the acid. This also agrees with the fact that trichloroacetic acid is a weaker acid in strongly differentiating alcohols than in levelling alcohols.

Thus the data obtained indicate that the probability of reaction of carboxylic acids with strongly differentiating alcohols is less than that for levelling alcohols. This can be related to the steric effects which must be taken into account in the reaction of carboxylic acids with differentiating solvents.

We studied the infrared spectra of CCl_3COOH and CCl_3COOD in anisole and dibutyl ether[98]. These data give information on the reaction of the carboxylic acid with solvents containing alkoxy-oxygen. Study of the spectra indicated that the hydrogen bond formed by ethers with the hydroxyl group of the acid is stronger than that formed by alcohols. The νOH bands for the acid monomers in ethers lie in the range 2800–3100 cm^{-1}. The corresponding νOD bands in ethers should be displaced towards lower frequencies[99,100]; they appear at 2180 cm^{-1} in dibutyl ether and at 2270 cm^{-1} in anisole. It can be seen from these data that the hydrogen bond formed by trichloroacetic acid with dibutyl ether is stronger than that formed with anisole. This agrees with the fact that dibutyl ether is a more basic solvent, that is, it has a stronger electron-donating power than anisole.

The bands observed in the range 2550–2600 cm^{-1} in the spectra of CCl_3COOH were assigned to the vibrations of the OH group of the acid dimers. In the spectra of CCl_3COOD in ethers the corresponding bands due to the vibrations of the OD bonds of the acid dimers lie in the range 2030–2060 cm^{-1}.

The frequency of the stretching vibrations of the C=O group of the acid in ethers at 1765–1770 cm^{-1} is slightly greater than that of the band in alcohols (1750 cm^{-1}); this can be attributed to the absence of the perturbing influence of the hydrogen bond on the carbonyl group.

Ginzburg and Abramovich[101], in a study of the reaction of trichloroacetic acid with ethers, showed that in equimolar mixtures of the acid and ethers in CCl_4 the absorption band of the carbonyl group of the acid dimers appears in the form of a shoulder. In our studies, carried out in ethers without an inert solvent, there was almost no trace of a band due to the acid dimers in this range. The presence of bands characteristic of hydrogen bonds formed by the OH (OD) group of the acid, however, indicates that the solutions studied contain some acid dimers. The relative concentration of dimers is greater in dibutyl ether than in anisole, that is, the probability of reaction of the acid with dibutyl ether is less than that for anisole, although the hydrogen bond formed by the trichloroacetic acid molecules with dibutyl ether is stronger than that formed with anisole. This agrees with the data obtained by Ginzburg and Abramovich[101], according to which dibutyl ether, in its reaction with trichloroacetic acid, appears to exhibit weaker electron-donating properties than propyl and ethyl isobutyl ethers. It may therefore be concluded that the relative decrease in the strength of trichloroacetic acid in dibutyl ether compared with anisole is due not so much to the strength of the hydrogen bond between the acid and the ether as to the probability of its formation.

We also recorded the infrared spectra of diethylammonium trichloroacetate in the alcohols studied[98]. No significant displacement of the band due to the asymmetric stretching vibrations of the carboxylate ion (1680 cm^{-1}) in different alcohols was observed. The difference in the

reactions of the trichloroacetate ion with alcohols apparently does not influence the frequency of the asymmetric stretching vibrations of the carboxylate ion.

2. Ketones

The strengths of many acids in acetone and aqueous acetone mixtures were studied by Izmailov and coworkers[9], using electrometric methods. They showed[102,103] that the differentiating action of acetone is due to the formation of a reaction product with 1 : 1 composition by the carboxylic acids and the ketone, in contrast to the product with the 1 : 2 composition obtained in water and alcohols[96,103,104].

The authors cited also showed that the differentiating action of acetone on the strength of acids is related to a decrease in the solvation energies of the anions of the carboxylic acids compared with their solvation energies in water. The solvation energies of the anions formed by nitrophenols in acetone differ comparatively little from their energies of solvation in water[105,106].

We used the buffer-free indicator method to study the strength of acids in various ketones, including acetone[25,107,108]. The pK values for acids in these solvents, and the values of ΔpK and Δ'pK, are given in Tables 13, 14, and 15 respectively.

Table 13. pK values for acids in ketones[25,107,108] and acetic anhydride[109].

Acids		Solvents				
		acetone	acetophenone	benzophenone	cyclohexanone	acetic anhydride
	DC	20.7	17.39	13.3	18.3	20.7
	°C	20±2	20±2	53±2	22±2	22±2
Formic		9.57	8.61	—	8.83	—
Monochloroacetic		9.21	8.31	—	8.16	8.73
Acetic		10.62	10.03	—	—	—
Dichloroacetic		7.70	7.41	7.96	6.85	7.84
Trichloroacetic		6.51	6.26	6.14	5.66	6.78
Propionic		—	10.07	—	—	—
Benzoic		—	9.80	—	—	—
Salicylic		9.08	8.14	—	8.01	—
o-Nitrobenzoic		—	8.14	—	8.23	—
m-Nitrobenzoic		—	8.62	—	8.68	—
p-Nitrobenzoic		—	8.72	—	8.70	—
α-Dinitrophenol		7.55	7.36	—	7.32	—
β-Dinitrophenol		7.77	7.47	—	7.33	—
Picric		4.14	4.55	5.29	4.24	5.97

The results (Tables 13–15) show that all the ketones which we studied are differentiating solvents. The basic strengths of the ketones studied are similar[90,110–112], but if we nevertheless arrange them in order of increasing basic strength—benzophenone < acetophenone < acetone < cyclohexanone—and compare the order with the order of the pK values for picric acid in the same solvents, we may conclude that the strength of picric acid increases in accordance with the increase in the basic properties of the ketone. The strengths of carboxylic acids in all the ketones decrease considerably compared with the values for water, and the decrease is much greater than that for nitrophenols.

The ketones which we studied exhibit similar differentiating properties, but when the methyl radicals in the acetone molecule are replaced by phenyl radicals (Table 15), the differentiating properties of the corresponding ketones decrease. Although the effect is weak, ketones apparently show steric effects in the reaction of the carboxylic acid dimers with the solvent. The fact that the influence of the radicals of the ketones on the differentiating properties of these solvents is slight can be attributed to the fact that the radicals in ketones are further removed from the oxygen than in alcohols and ethers.

Table 14. ΔpK values for acids.

Acids	Solvents				
	acetone	acetophenone	benzophenone	cyclohexanone	acetic anhydride
Formic	5.82	4.89	—	5.08	—
Acetic	5.86	5.27	—	—	—
Monochloroacetic	6.34	5.43	—	5.29	5.86
Dichloroacetic	6.40	6.11	6.66	5.55	6.54
Trichloroacetic	5.81	5.56	5.44	4.96	6.08
Propionic	—	5.20	—	—	—
Benzoic	—	5.60	—	—	—
Salicylic	6.11	5.17	—	5.01	—
o-Nitrobenzoic	—	5.98	—	6.07	—
m-Nitrobenzoic	—	5.13	—	5.19	—
p-Nitrobenzoic	—	5.32	—	5.30	—
α-Dinitrophenol	3.53	3.34	—	3.30	—
β-Dinitrophenol	3.97	3.68	—	3.53	—
Picric	3.64	3.75	4.49	3.44	5.17

To investigate the influence of differences in the solvation of the anions of acids of different character on the differentiating properties of ketones, we studied the heats of dissolution of diethylammonium salts in cyclohexanone. The results (Table 9) show that in cyclohexanone, as in acetone, there is a relatively greater decrease in the solvation energy of the anions of carboxylic acids, compared with the anions of nitrophenols, on going from water to the ketone.

Table 15. Differentiating action of ketones and acetic anhydride.

Solvent	Δ'pK
Acetone	2.5
Acetophenone	1.7
Benzophenone	1.3
Cyclohexanone	1.6
Acetic anhydride	1.1

All the ketones studied are differentiating solvents and can be used in non-aqueous titration.

Tables 13–15 also give data on the strength of acids in acetic anhydride[109] and its differentiating properties. The data show that acetic anhydride is a differentiating solvent, although its differentiating action is weaker than that of ketones. Because of the acidic properties of acetic anhydride, acids dissolved in this solvent are slightly weaker than in ketones.

Table 16. Values of pK_{tr} and pK_{diss} for acids in esters.

Acids		Solvents												
		water	butyl acetate (Ref.120)	ethyl acetate (Ref.118)	benzyl acetate (Ref.118)	phenyl acetate (Ref.119)	ethyl monochloroacetate (Ref.119)	acetoacetic ester (Ref.119)	diethyl carbonate (Ref.119)	ethylbenzoate (Ref.118)	Acetone-benzene (Ref.119)	tributyl phosphate (Refs.119,120)	triphenyl phosphate (Ref.120)	tricresyl phosphate (Ref.121)
	DC	81.0	5.01	6.02	5.10	5.38	20	15.7	2.82	6.06	6.02	7.97	—	6.7
	°C	25	20±2	22±2	22±2	22±2	22±2	22±2	22±2	22±2	22±2	20±2	49±2	20±2
		pK_{diss}	pK_{tr}	pK_{tr}	pK_{tr}	pK_{tr}	pK_{diss}	pK_{diss}	pK_{tr}	pK_{tr}	pK_{tr}	pK_{tr}	pK_{tr}	pK_{tr}
Trichloroacetic		0.70	1.14	1.60	2.57	1.51	6.57	6.28	2.52	1.92	1.55	3.32	2.69	—
Dichloroacetic		1.30	3.86	3.08	3.75	3.06	—	7.48	4.30	—	2.87	4.44	2.25	3 62
Monochloroacetic		2.87	4.98	4.78	5.63	4.00	8.81	9.04	5.77	5.34	4.48	5.32	—	—
Acetic		4.76	—	—	—	—	—	10.84	—	—	6.07	—	—	—
Formic		3.75	—	5.91	6.29	—	—	9.66	6.23	6.06	5.06	4.09	—	—
Salicylic		2.97	5.04	4.42	5.38	—	8.73	8.24	3,22	5.35	4.11	5.07	—	—
Benzoic		4.20	—	—	—	—	—	10.62	—	—	5.66	—	—	—
m-Nitrobenzoic		3.49	—	4.95	6.18	—	—	9.40	—	5.81	4.82	3.85	—	—
p-Nitrobenzoic		3.40	—	—	6.03	—	—	9.37	—	—	4.85	3.88	—	—
o-Nitrobenzoic		2.20	—	—	—	—	8.87	9.36	5.10	—	4.26	—	—	—
Picric		0.80	0.69	1.12	1.82	1.33	—	4.64	1.77	1.60	1.39	0.43	1.31	1.11
α-Nitrophenol		4.02	4.64	4.18	5.54	—	8.84	8.25	5.92	5.51	4.26	4.01	—	—
β-Nitrophenol		3.80	4.66	3.97	5.21	—	8.84	8.68	5.15	5.01	3.64	4.04	—	—
Hydrochloric		0.8		—	—	—	—	—	—	—	—	1.21	—	—
Sulphuric		—3.0	—	—	—	—	—	—	—	—	—	1.46	—	—

3. Esters

Esters are solvents which contain a carbonyl group, like ketones, but they also contain alkoxy-oxygen, that is, they have a compound functional group.

Most workers[113-117] consider that esters react with acids chiefly through the carbonyl oxygen, but some authors[114-116] conclude that reaction between the acids and the alkoxy-oxygen of the ester is also possible.

Esters form reaction products with the 1 : 1 composition both with acids and with nitrophenols[113]. According to Izmailov's theory, esters should be differentiating solvents. The oxygen atoms in the ester molecule, however, may be screened to some extent by the radicals, so that steric effects may be observed in the reaction with carboxylic acid dimers. It is therefore to be expected that esters with different radicals and different structures may show varying differentiating properties.

We studied the strength of acids (chiefly carboxylic acids and nitrophenols)[118-121] in eleven esters and an acetone–benzene mixture with an acetone mole fraction of 0.305 (DC = 6)[122]. The strengths of the acids were determined by the buffer-free indicator methods described above. In most of the esters with low DC which we studied, we determined the transformation constants of the acids and the indicators; in two esters with larger DC values (ethyl monochloroacetate and acetoacetic ester) we determined the dissociation constants of the acids. The results are given in Table 16.

The strengths of the acids depend on the basic strength of the solvent. The basic nature of the esters was studied by various methods: from the ionisation potentials[123-128], the solubility of HCl[59,60], the shifts in the infrared spectra on reaction with the OD group of methanol[90,92,129-132], and the Taft constants[133].

On the basis of published data, the esters which we studied can be arranged in order of decreasing basic strength. This order is given in Table 17, which also gives the values of pK for the transformation of picric and trichloroacetic acids.

Table 17.

	Esters	pK_{tr} for picric acid	pK_{tr} for trichloroacetic acid
decreasing basic nature ↓	Tributyl phosphate	0.44	3.32
	Butyl acetate	0.70	1.14
	Tricresyl phosphate	1.11	—
	Ethyl acetate	1.12	1.60
	Triphenyl phosphate	1.31	2.69
	Phenyl acetate	1.33	1.51
	Ethyl benzoate	1.60	1.92
	Diethyl carbonate	1.77	2.54
	Benzyl acetate	1.82	2.57
	Acetoacetic ester	4.65	6.28

With decrease in the basic strength of the esters there is an increase in the value of pK for picric acid, that is, a decrease in its strength (Table 17). This relationship is not observed for trichloroacetic acid. For example, in the most basic ester—tributyl phosphate—pK_{tr} for trichloroacetic acid is greater than the values in other esters which are less basic. Thus the change in the strength of nitrophenols in esters is related chiefly to the basic nature of these solvents, whereas the strengths of carboxylic acids are determined not only by the basic nature of the ester, but also by other factors.

In all esters, the decrease in the strengths of carboxylic acids on going from water to the ester is greater than the decrease in the strengths of the nitrophenols. This characterises the esters as differentiating solvents. The differentiating action of esters is illustrated by Table 18, which gives the $\Delta' pK$ values determined graphically from the data in Table 16. The results show that the differentiating action of the esters which we studied on the strength of acids varies between different esters (Table 18). The differentiating action of esters does not depend on their dielectric constant.

Although the esters of acetic acid have similar dielectric constants, their differentiating properties differ considerably. The differentiating action of diethyl carbonate—an

ester with low dielectric constant—on the strength of acids is similar to that of ethyl acetate—a solvent with high dielectric constant. Acetoacetic ester, with high DC, is a strongly differentiating solvent.

Examination of Table 18 shows that the differentiating properties of esters depend on the nature and spatial complexity of the radical of the alcohol group.

Table 18. Differentiating action of esters.

Solvents	DC	$\Delta' pK_{tr}$	Solvents	DC	$\Delta' pK_{tr}$
Butyl acetate	5.01	2.0	Benzene + acetone	6.02	1.2
Benzyl acetate	5.10	1.4	Tributyl phosphate	7.97	3.2
Ethyl acetate	6.02	1.6	Triphenyl phosphate	—	1.4*
Phenyl acetate	5.35	0.6			$\Delta' pK$
Diethyl carbonate	2.82	1.6	Acetoacetic ester	15.70	2.0
Ethyl benzoate	6.02	1.2	Ethyl monochloroacetate	20.00	0.8

* Estimated from data in Table 17.

The data in Table 16 show that the strengths of carboxylic acids in esters of acetic acid decrease with increase in the spatial complexity of the alkoxy-radical. In accordance with this, the differentiating properties of these solvents decrease in the order: butyl acetate > ethyl acetate > benzyl acetate > phenyl acetate. Thus the reaction of carboxylic acids with esters is influenced by steric effects depending on the size and complexity of the alkyl radical.

Ethyl acetate and diethyl carbonate exhibit the same differentiating action on the strengths of carboxylic acids and nitrophenols. It may be assumed that the identical differentiating action is determined by the identical degree of screening of the functional groups of the ester in these compounds.

Ethyl benzoate is a slightly weaker differentiating solvent than diethyl carbonate and ethyl acetate, since its acidic group contains the planar phenyl radical. Ethyl monochloroacetate is a weak differentiating solvent. This can apparently be attributed to the reduced electron-donating power of its functional group associated with the presence of the chlorine atom in its molecule[134,135].

The data in Table 16 show that the strengths of not only carboxylic acids, but also nitrophenols, are low in ethyl monochloroacetate, compared with ethyl acetate and other esters of carboxylic acids. We also studied the differentiating properties of acetoacetic ester (Table 16), which under ordinary conditions contains keto- and enol-forms. In pure acetoacetic ester under normal conditions, the keto form predominates (93%). This ester is a strongly differentiating solvent (Table 18). We purified acetoacetic ester in an all-glass distillation apparatus. These distillation conditions, and also the addition of acids, displace the equilibrium towards the formation of the enol form. In the liquid state, as a result of intramolecular hydrogen bonding, the enol form is present as a chelate compound[136] in which there is particularly strong steric hindrance to the reaction with carboxylic acid dimers. This is apparently also responsible for the differentiating properties of acetoacetic ester.

Esters of phosphoric acid can be arranged in the following order of decreasing differentiating properties: tributyl phosphate > tricresyl phosphate > triphenyl phosphate. The fact that tributyl phosphate has the strongest differentiating action can be attributed to the spatial complexity of its molecule, resulting from the large butyl radicals arranged at the apices of a tetrahedron[137,138]. In triphenyl phosphate the planar phenyl radicals also lie at the apices of a tetrahedron, but in contrast to the situation in tributyl phosphate, the axes of the phenyl radicals are parallel to one another[139]. This is apparently responsible for the fact that the steric hindrance to the reaction with carboxylic acid dimers is less for triphenyl phosphate than for tributyl phosphate.

Tributyl phosphate exhibits specific differentiating properties. Differentiation within the class of carboxylic acids is observed in this solvent: the chloroacetic acids are weaker than the nitrobenzoic acids. The behaviour of mineral acids in tributyl phosphate is also unusual: in this solvent, hydrochloric and sulphuric acids are weaker than picric acid[120]. In accordance with published data[140,141], we regarded sulphuric acid in tributyl phosphate as a monobasic acid. The transformation constants which we obtained[120] by the indicator method for hydrochloric and sulphuric acids in tributyl phosphate are close to one another. Hesford and McKay[142] determined the dissociation constants of these acids in tributyl phosphate from their electrical conductivities. The values which they obtained are also close to one another. The first dissociation constant of sulphuric acid was calculated.

The replacement of the butyl radicals by cresyl or phenyl radicals in the phosphoric acid ester leads to a decrease in the differentiating power of the solvent.

The stronger differentiating action of the esters of phosphoric acid compared with the esters of acetic acid can be attributed both to the structure of the molecules of the phosphoric acid esters and to the nature of phosphoric acid. The molecules of the esters of phosphoric acid have a tetrahedral shape, in which one of the apices is occupied by the phosphoryl oxygen, whereas the molecules of the esters of acetic acid have a planar structure, with *cis*-arrangement of the radicals[143].

Table 19. Integral heats of dissolution of salts[120,121] at a dilution of 1:400 (27°C).

Diethylammonium salts	ΔH, kcal mole^{-1}		
	water	benzyl acetate	tributyl phosphate
Picrate	4.8	5.0	3.1
β-Dinitrophenolate	4.7	6.9	2.5
Benzoate	insol.	2.5	10.9
Salicylate	2.8	4.0	3.8
Trichloroacetate	1.8	6.6	6.8
Acetate	—0.8	3.9	9.1

To estimate the influence of the solvation of the anions of the acids by different esters on the differentiating properties of the latter, we determined the integral heats of dissolution of the diethylammonium salts of various carboxylic acids and nitrophenols in benzyl acetate (a weakly differentiating solvent) and tributyl phosphate (the strongest differentiating solvent)[120,121]. The results (Table 19) show that the solvation of the anions of carboxylic acids in esters is much more endothermic than that in water. The solvation of the anions of nitrophenols in benzyl acetate is

slightly less exothermic than that in water, whereas in tributyl phosphate the opposite relationship is observed.

Comparison of the heats of solvation of the anions of the acids in the two esters (Table 19) indicates that the difference in the differentiating action on the strength of acids shown by tributyl phosphate and benzyl acetate is related not only to the factors examined above but also to a difference in the solvation of the anions of the carboxylic acids. The decrease in the solvation of the anions of the carboxylic acids in tributyl phosphate can be attributed to steric effects in the reaction of these anions with the ester.

Thus the differentiating action of esters depends on steric effects produced in the reaction of their molecules with both the molecules and the anions of carboxylic acids.

On the basis of our studies, esters can be recommended as differentiating solvents for the titration of acids.

Tributyl phosphate is a specific differentiating solvent. Picric acid and trichloroacetic acid can be determined separately in the presence of one another in this solvent. In this solvent it is also possible to determine separately chloroacetic and nitrobenzoic acids, which have similar strengths in water. This has been confirmed by our experiments [121] on colorimetric and high-frequency titration.

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The change in the strength of acids of different character on going from water to oxygen-containing solvents (alcohols, ketones, ethers, and esters) depends on steric effects in the reaction of the molecules and anions of the acids with the solvent molecules. Increase in the spatial complexity of the solvent molecules and increase in the screening of the oxygen of the functional group lead to a relative decrease in the strengths of carboxylic acids; this is responsible for the differentiating action on the strength of acids in a given solvent.

Steric factors are particularly important in the reaction of carboxylic acid dimers with the alkoxy-oxygen of the solvents (alcohols and ethers).

The differentiating action of primary alcohols depends little on the size and degree of branching of their radical. Secondary and tertiary alcohols have a stronger differentiating action on the strength of acids than primary alcohols.

Ethers with sterically simple radicals (diphenyl oxide and anisole) are almost levelling solvents. The differentiating action of ethers with saturated radicals on the strength of acids increases considerably with increase in the size and complexity of their radicals.

The difference in the strengths of carboxylic acids in solvents containing alkoxy-oxygen is determined not so much by the basic nature of the solvent and hence the strength of the hydrogen bond formed as a result of the reaction of the carboxylic acid dimers with the molecules (in the case of alcohols, with the molecular associates) of the solvent as by the probability of formation of this bond, which depends on steric factors.

Ketones and esters are differentiating solvents, but the differentiating properties of these compounds also depend on the spatial complexity of their molecules and are determined by the relative decrease in the strength of carboxylic acids in these solvents.

Examination of the behaviour of the acids which we have studied in oxygen-containing solvents leads to the general conclusion that the strengths of acids in solvents depend on the spatial complexity of both the molecules and the ions of the acid and the molecules of the solvent. The differentiating properties of a solvent are determined to a considerable extent by steric effects in the reaction of the electrolyte with the solvent.

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