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KINETIC NEUTRAL-SALT EFFECTS OF ORGANIC SALTS ON THE ALKALINE HYDROLYSIS OF METHYL-1-NAPHTHOATE*

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(Contribution from the Chemistry Department of Florida State University)

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Abstract—The reaction of methyl-1-naphthoate with hydroxide ion in 50·0 wt. % dioxane–water follows second-order kinetics and shows the following neutral-salt effects: (1) Alkali halide salts such as NaCl produce small and nearly colligative retardations. (2) Salts with organic anions such as sodium tetraphenylboride produce large and specific retardations. (3) Salts with organic cations such as $(n\text{-}C_4H_9)_4NI$ produce specific effects that range from barely significant retardations to marked accelerations. Detergent salts such as sodium lauryl sulphate produce specific effects that are characteristic of the organic ion. Hydrocarbons such as naphthalene or cyclohexane produce specific retardations that are comparable (per mole) to those produced by salts with structurally similar organic anions. NaCl, $NaB(C_6H_5)_4$ and $(CH_3)_4NCl$ produce characteristically different salt effects on the activation parameters. Spectral measurements of solutions of methyl-1-naphthoate and $NaB(C_6H_5)_4$ fail to show any significant interaction absorption.

The results suggest the theory that methyl-1-naphthoate forms loose Van der Waals complexes with the added organic species. If the complexes bear a negative charge (organic anions), attack by hydroxide ion is impeded; if they bear a positive charge, attack is facilitated. The specific manner in which the neutral-salt effects vary with the structure of the organic species suggests that the dominant interactions leading to complex formation involve London dispersion forces.

IN MOST organic reactions, the effects of neutral salts on the rate constant are much too complex to be consistent with any simple theoretical model. In the occasional reaction where a simple model will reproduce the facts, the fit of the model is likely to be limited to common inorganic salts such as the alkali halides. For example, in the hydrolysis of *t*-butyl chloride in water,[1] the effects of most inorganic salts on the rate constant are colligative, as required by Ingold's ion atmosphere model,[2] but there are specific exceptions.[1] In the hydrolysis of neophyl *p*-toluenesulphonate in 50·0 wt. % dioxan–water,[3] the effects of many inorganic salts on the rate constant run parallel to their effects on the activity of the solvent components, as required by the theory of salt-induced medium effects,[4] but again there are specific exceptions. Salts with organic ions (which are always polyatomic, and usually consist of ten or more atoms) are likely to produce effects that deviate from whatever pattern is "normal" for the common inorganic salts.

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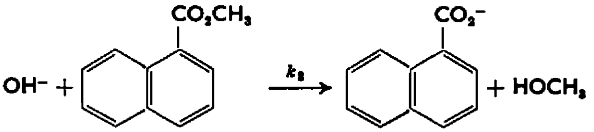
[1] G. A. Clarke and R. W. Taft, *J. Amer. Chem. Soc.* **84**, 2295 (1962).

[2] L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.* 979 (1940).

[3] E. F. J. Duynstee, E. Grunwald and M. L. Kaplan, *J. Amer. Chem. Soc.* **82**, 5654 (1960).

[4] E. Grunwald and A. F. Butler, *J. Amer. Chem. Soc.* **82**, 5647 (1960).

We now report kinetic salt effects for a wide variety of organic and inorganic salts on the alkaline hydrolysis of methyl-1-naphthoate in 50·0 wt. % dioxan–water at 25·0°.



(1)

This reaction follows second-order kinetics. Addition of alkali halide salts produces a small and nearly colligative decrease in k_2. Salts with organic cations, such as $(C_4H_9)_4N^+$ or $C_6H_5N(CH_3)_3^+$, produce a slight-to-fairly large increase in k_2. Salts with organic anions, such as 1-naphthoate ion or $(C_6H_5)_4B^-$, produce a substantial decrease in k_2. The effects of organic detergent salts are similar to those of other organic salts: 0·017 M lauryltrimethylammonium chloride produces a slight acceleration, sodium lauryl sulphate produces a substantial deceleration. Hydrocarbons, such as naphthalene or *cis*-decalin, produce a substantial deceleration.

RESULTS

Salt effects. Experiments showing the effect of salts and nonelectrolytes on the second-order rate constant, k_2, of reaction (1) are summarized in Table 1. The initial concentrations of the reactants were 0·009 M. Each measurement of k_2 was accompanied by a control experiment, conducted under the same conditions but without added solute, which gave a value for the reference rate constant, $k_2°$. Data

Table 1. Effects of salts and nonelectrolytes on the alkaline hydrolysis of methyl-1-naphthoate in 50 wt. % dioxan–water at 25·0°

Solute	Concentration (moles/liter)	ln $k_2/k_2°$
$2\text{-}C_{10}H_7N(CH_3)_3Cl$	0·0211	0·086
	0·0424	0·104
	0·0776	0·095
$C_6H_5N(CH_3)_3Cl$	0·0726	0·148
	0·1628	0·207
$(n\text{-}C_4H_9)_4NI$	0·0512	0·049
	0·1351	0·030
$C_{12}H_{25}(CH_3)_3NCl$	0·0168	0·010
	0·0302	0·000
	0·1046	−0·118
$(CH_3)_4NCl$	0·0578	−0·018
	0·0958	−0·012
	0·1863	−0·006
	0·3785	−0·010
NaOH	0·0319	0·039
	0·0734	0·010
KCl	0·0694	−0·110
	0·2189	−0·192
KBr	0·0467	−0·056
	0·0906	−0·079
	0·2306	−0·167

TABLE 1 (*contd*)

Solute	Concentration (moles/liter)	$\ln k_2/k_2^0$
KI	0·0972	−0·124
	0·1841	−0·157
$KClO_4$	0·0150	0·000
	0·0288	−0·056
	0·0542	−0·084
NaCl	0·0708	−0·103
	0·1258	−0·157
	0·2226	−0·203
	0·4417	−0·357
$NaNO_3$	0·2033	−0·259
$NaClO_4$	0·0574	−0·155
	0·1148	−0·208
	0·1716	−0·290
	0·2407	−0·333
	0·3959	−0·387
$2\text{-}C_{10}H_7SO_3Na$	0·0252	−0·054
	0·0428	−0·083
	0·0710	−0·140
	0·1505	−0·243
$p\text{-}BrC_6H_4SO_3Na$	0·0522	−0·140
	0·0910	−0·214
$1\text{-}C_{10}H_7CO_2Na$	0·0113	−0·041
	0·0281	−0·092
	0·0415	−0·110
$NaSO_4C_{12}H_{25}$[a]	0·0155	−0·137
	0·0378	−0·284
$NaB(C_6H_5)_4$	0·0153[b]	−0·170
	0·0161[c]	−0·180
	0·0265[c]	−0·304
	0·0304[b]	−0·289
	0·0345[c]	−0·335
$1\text{-}C_{10}H_7CO_2CH_3$	0·0171	−0·036
	0·0327	−0·081
$C_{10}H_8$	0·0179	−0·102
	0·0301	−0·108
	0·0380	−0·150
cis-$C_{10}H_{18}$[d]	0·0253	−0·115
C_6H_6[d]	0·0988	−0·095
C_6H_{12}[d]	0·0985	−0·163
dioxan	1·18[e]	−0·155

[a] We are very much obliged to Professor K. J. Mysels for providing an especially purified sample of sodium lauryl sulphate.

[b] A sample from Fa. Heyl and Co was used.

[c] A sample from Baker Chemical Co. was used.

[d] Measured in 65·0 wt. % dioxan–water.

[e] This is the difference in molar concentration of dioxan between 50 and 55 wt. % dioxan–water.

concerning $k_2°$ are listed in Table 2. It has been shown, from pressure and e.m.f. data, that salts are largely dissociated to free ions in 50·0 wt. % dioxan–water at the concentrations employed in this work.[5]

For a reaction between an ion and a nonelectrolyte, the effect of added salt on the second-order rate constant can be represented as a power series expansion in the added salt concentration, c, as shown in Eq. (2).

$$\ln (k_2/k_2°) = Ac + Bc^{3/2} + Cc^2 + Dc^{5/2} + \ldots \tag{2}$$

Equation (2) can be derived from a general expression for the free energy of a homogeneous mixture of electrolytes and nonelectrolytes, due to Scatchard and Prentiss,[6] provided that two assumptions are made: (1) The concentration of the reactants is small compared to that of the added salt; (2) $k_2/k_2°$ is related to molar activity coefficients, f, according to Eq. (3), which can be derived

$$k_2/k_2° = f_{\text{ester}} \cdot f_{\text{OH}^-}/f_{\text{transition state complex}} \tag{3}$$

from transition-state theory. According to Eq. (2), the plot of ln $(k_2/k_2°)$ versus c becomes linear at low concentrations of added salt.

TABLE 2. KINETIC RESULTS FOR THE ALKALINE HYDROLYSIS OF METHYL-1-NAPHTHOATE IN DIOXAN–WATER MIXTURES

Wt % dioxan in solvent	$10^4 k_2°$(M^{-1} sec.$^{-1}$.)[a] 0·00°	25·00°	50·00°	ΔH≠ (kcal)	ΔS≠ (e.u.)
40	9·53[b]	69·7	384	$12{\cdot}3_7$	−26·9
45	7·95[b]	61·2	346	$12{\cdot}6_4$	−26·2
50	6·95	54·1	304	$12{\cdot}7_6$	−26·4
55	6·00[b]	47·3	289[b]	$12{\cdot}9_9$	−25·5
60	5·10[b]	43·2	264	$13{\cdot}2_5$	−24·9
65	4·92[b]	40·2	250[b]	$13{\cdot}1_8$	−25·2

[a] Rate constants are based on two or more independent experiments, except where noted.
[b] Only one run.

Within the experimental error of ±0·02 ln unit, plots of ln $(k_2/k_2°)$ versus c constructed from the data in Table 1 show, with few exceptions, only moderate curvature. That is, most plots show with high probability that the term proportional to c in Eq. (2) makes the dominant contribution to the observed effect. The probable exceptions involve the following organic-cation salts: $2\text{-}C_{10}H_7N(CH_3)_3Cl$, $(n\text{-}C_4H_9)_4NI$, and $n\text{-}C_{12}H_{25}N(CH_3)_3Cl$. Here the effects observed at the highest concentrations seem to be dominated by terms involving c to a fairly high power, and it is possible that micelle formation takes place. Because of the relatively large experimental error, the preceding summary must be regarded as involving statements of reasonably high probability, rather than established facts.

The coefficient, A, in Eq. (2) is equal to $\partial \ln k_2/\partial c$ when $c = 0$, and therefore measures the response of k_2 to addition of salt in highly dilute solution. Values of

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[5] [a] E. Grunwald, G. Baughman and G. Kohnstam, *J. Amer. Chem. Soc.* **82**, 5801 (1960); [b] A. F. Butler and E. Grunwald, *J. Phys. Chem.* **67**, 2330 (1963).

[6] G. Scatchard and S. S. Prentiss, *J. Amer. Chem. Soc.* **56**, 1486 (1934); *Ibid.* **56**, 2320 (1934).

this coefficient have been estimated from the data in Table 1 and are summarized in Table 3. We should like to divide these values into four groups.

(1) For the common alkali halide salts, the values of $\partial \ln k_2/\partial c$ are quite non-specific. A single value, −1·5, represents all data within experimental error.

(2) For halide salts with organic cations, the values of $\partial \ln k_2/\partial c$ are significantly greater (in the algebraic sense) than −1·5. If the cation in a quaternary ammonium salt contains an aryl group, $\partial \ln k_2/\partial c$ is greater than for an analogous salt that contains only alkyl groups.

TABLE 3. EFFECT OF ADDED SOLUTES ON THE RATE CONSTANT FOR THE ALKALINE HYDROLYSIS OF METHYL-1-NAPHTHOATE IN 50 WT % DIOXAN–WATER AT 25°

Solute	$\left(\frac{\partial \ln k_2}{\partial c}\right)_{c=0}$	Solute	$\left(\frac{\partial \ln k_2}{\partial c}\right)_{c=0}$
1. KCl	−1·6	4. $KClO_4$	−1·5
KBr	−1·2	$NaClO_4$	−2·7
KI	−1·5	$NaNO_3$	−2
NaCl	−1·7	NaOH	−0·6
2. $(CH_3)_4NCl$	−0·1	5. 1-$C_{10}H_7CO_2CH_3$	−2·3
(n-$C_4H_9)_4NI$	+0·8	$C_{10}H_8$	−4·0
n-$C_{12}H_{25}N(CH_3)_3Cl$	+0·2	cis-$C_{10}H_{18}$[a]	−4·5
$C_6H_5N(CH_3)_3Cl$	+2·3	C_6H_6[a]	−1·0
2-$C_{10}H_7N(CH_3)_3Cl$	+4	C_6H_{12}[a]	−1·7
		dioxan	−0·1
3. 2-$C_{10}H_7SO_3Na$	−2·0		
p-$BrC_6H_4SO_3Na$	−2·5		
1-$C_{10}H_7CO_2Na$	−3·2		
n-$C_{12}H_{25}OSO_3Na$	−8		
$(C_6H_5)_4BNa$	−11		

[a] Measured in 65·0 wt % dioxan

(3) For sodium salts with organic anions, the values of $\partial \ln k_2/\partial c$ are significantly smaller (in the algebraic sense) than −1·5. For anions that contain a naphthyl group, the values are similar to those observed for nonelectrolyte naphthalene derivatives (Table 3, 5). For some of the other organic anions, the negative salt effects are strikingly large.

(4) Inorganic alkali salts with anions of more complex structure produce effects of greater specificity than do the alkali halide salts. We shall not attempt to rationalize these results.

Micelle formation. We shall suggest in the Discussion that the organic-ion salt effects involve molecular interactions similar to those that cause micelle formation in aqueous solutions of detergent salts. It is therefore of interest to find out whether micelle formation is greatly attenuated in 50 wt. % dioxan–water.

For $(CH_3)_4NCl$ and $NaB(C_6H_5)_4$, it is clear from vapour pressure data[5a] that micelle formation is insignificant in 50 wt. % dioxan–water up to concentrations of these salts of at least 0·05 M. Since the plots of ln (k_2/k_2°) versus c for these salts are also quite linear (data in Table 1), it is probable that micelle formation is negligible also under the conditions of the present experiments.

On the other hand, certain organic-cation salts do give curved plots of ln (k_2/k_2°) versus c at the higher experimental concentrations, as mentioned in the preceding section. The data permit the interpretation that the critical micelle concentration falls within the experimental concentration range.

In this connection it is instructive to consider some data obtained by Kaplan and Grunwald.[7] These workers studied the effect of 0·1 M detergent salts on the solubility and rate constant for hydrolysis of neophyl *p*-toluenesulphonate in 50 wt. % dioxan–water. Their results are summarized in Table 4. It is seen that the addition of either a cationic or an anionic detergent salt produces a large effect on both properties. The magnitude of the effect suggests that a micelle phase is formed in which neophyl tosylate is not only quite soluble but also quite unreactive toward hydrolysis.

TABLE 4. EFFECT OF DETERGENT SALTS ON SOLUBILITY AND HYDROLYSIS RATE OF NEOPHYL *p*-TOLUENESULPHONATE IN 50·0 WT. % DIOXAN[a]

Detergent salt	Solubility (M) 25·0°	$10^7 k_1(\text{sec.}^{-1})$[c] 25·0°	50·0°	Ratio at 25° Solubility	k_1
None	0·0105	2·67	70·1	1·00	1·00
0·0948 M NaLS[b,d]	0·0241	1·26	36·5	0·44	0·47
0·0976 M CTABr[b,d]	0·0208	1·52	44	0·51	0·57

[a] Data of M. L. Kaplan and E. Grunwald.

[b] NaLS = sodium lauryl sulphate; CTABr = cetyl-trimethylammonium bromide.

[c] k_1 = first-order rate constant for hydrolysis. In the case of NaLS, a small correction was made for the hydrolysis of NaLS. In the case of CTABr, the values of t^{-1} ln (c_0/c) increased with time by about 25 % during the period of observation, one half-life, and k_1 was obtained by extrapolation to zero time.

[d] Solvolysis rates of 0·1 M NaLS and of 0·1 M CTABr in neutral 50% dioxan–water were indetectably small during four days at 50°. In the presence of 0·01 M toluenesulphonic acid catalyst, the pseudo-first order rate constant for solvolysis of 0·1 M NaLS was $1{\cdot}3 \times 10^{-7}$ sec^{-1} at 50° in 50% dioxan–water. There was no evidence for acid catalysis of the solvolysis of CTABr.

TABLE 5. SPECTRAL STUDIES OF METHYL-1-NAPHTHOATE AND SODIUM TETRAPHENYLBORIDE IN 50·0 WT. % DIOXAN–WATER AT 23°

Wavelength mμ	Extinction coefficient (M^{-1} cm^{-1}) ester	$NaB(C_6H_5)_4$	9·05 mM ester + 9·90 mM $NaB(C_6H_5)_4$ O.D. (obs.)[a]	O.D. (calc.)[b]
296	6370	0	0·594	0·577
274	3550	2350	0·548	0·555
266	2090	3300	0·523	0·516
253	1180	5100	0·594	0·612

[a] Optical path = 1 mm.

[b] Calc. from the extinction coefficients for the separate solutes and the solute conc.

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[7] M. L. Kaplan and E. Grunwald, measurements made at Florida State University in 1960. Experimental methods similar to those reported in Ref. 3.

This behaviour is completely analogous to the behaviour of organic substrates when detergent salts are added to their solution in pure water.[8–10]

In conclusion, the balance of evidence indicates that those interactions that cause micelle formation in water are still important in 50 wt. % dioxan–water.

Spectral studies. The very large negative kinetic salt effect of $NaB(C_6H_5)_4$ made it interesting to investigate whether spectroscopic evidence for interaction absorption between tetraphenylboride ion and methyl-1-naphthoate could be obtained. The UV absorption spectrum of a solution of methyl-1-naphthoate in 50 wt. % dioxan–water has two characteristic points, a maximum at 296 mμ and a minimum at 253 mμ. The spectrum of a solution of $NaB(C_6H_5)_4$ in 50 wt. % dioxan–water shows two maxima, one at 274 mμ and one at 266 mμ. Beer's Law is obeyed by both solutes at all four wavelengths up to concentrations of a few hundredths molar. Extinction coefficients are listed in Table 5. When methyl-1-naphthoate and $NaB(C_6H_5)_4$ are present in the same solution, the observed optical densities are in good agreement with optical densities calculated from the known concentrations and extinction coefficients, that is, there is no evidence for interaction absorption. (See last two columns of Table 5.) For the solution on which the optical density measurements were made, k_2/k_2° is predicted (by interpolation) to be 0·89, and solute-solute interaction should therefore be significant. The fact that interaction absorption was not observed suggests that any solute–solute complexes in the solution must be stabilized by such a mechanism that the electronic systems of the interacting molecules are perturbed only slightly.

Effect of solvent composition. Rate constants for reaction (1) were measured in dioxan–water mixtures containing from 40 to 65 wt. % of dioxan at 0°, 25° and 50°. The results are summarized in Table 2. The sensitivity of $\ln k_2^\circ$ to change in solvent composition is very slight—only about one fourth as large as that reported previously[3] for the hydrolysis of neophyl *p*-toluenesulphonate in dioxan–water mixtures. As a result, the contribution of salt-induced medium effects[3,4] to the observed salt effects should be quite small. Plots of $\ln (k_2^\circ/T)$ versus $1/T$ gave good straight lines at all solvent compositions. The resulting values of the activation parameters (Table 2) define an approximate isokinetic line.[11]

Activation parameters for salt effects. Kinetic salt effects for NaCl, $(CH_3)_4NCl$ and $NaB(C_6H_5)_4$ were measured in 50·0 wt. % dioxan–water at 0°, 25° and 50°. Analysis of the temperature coefficients of the salt effects confirms the previous conclusion, based on the data in Table 3, that there are fundamental differences in the mode of interaction of the three salts. Plots of $\ln (k_2/T)$ versus $1/T$ are nicely rectilinear for solutions containing NaCl or $(CH_3)_4NCl$, but become increasingly curved with increasing concentration of $NaB(C_6H_5)_4$. Activation parameters applying to the average temperature (25°) were calculated from the slopes and intercepts of the least-squares straight lines that give "best fit" to the data for each salt concentration. The results are shown in Fig. 1, which represents each salt effect by a point in the

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[8] E. F. J. Duynstee and E. Grunwald, *J. Amer. Chem. Soc.* **81**, 4540, 4542 (1959).

[9] [a] J. L. Kurz, *J. Phys. Chem.* **66**, 2239 (1962); [b] K. G. van Senden and C. Koningsberger, *Tetrahedron Letters* No. 1, 7 (1960).

[10] M. T. A. Behme and E. H. Cordes, *J. Amer. Chem. Soc.* **87**, 260 (1965); M. T. A. Behme, J. G. Fullington, R. Noel and E. H. Cordes, *Ibid.* **87**, 266 (1965).

[11] J. E. Leffler, *J. Org. Chem.* **20**, 1202 (1955).

$\Delta H^{\neq} - \Delta S^{\neq}$ plane. The uncertainty in the position of a point due to experimental error is shown by the highly eccentric ellipse drawn around the point for 0·00 M. The error contour to be drawn around any other point is an ellipse of similar size and equal inclination with respect to the co-ordinate axes.

Within experimental error, the activation parameters obtained with increasing NaCl concentration seem to define a straight line with a slope, β, of about $-40°$ K.

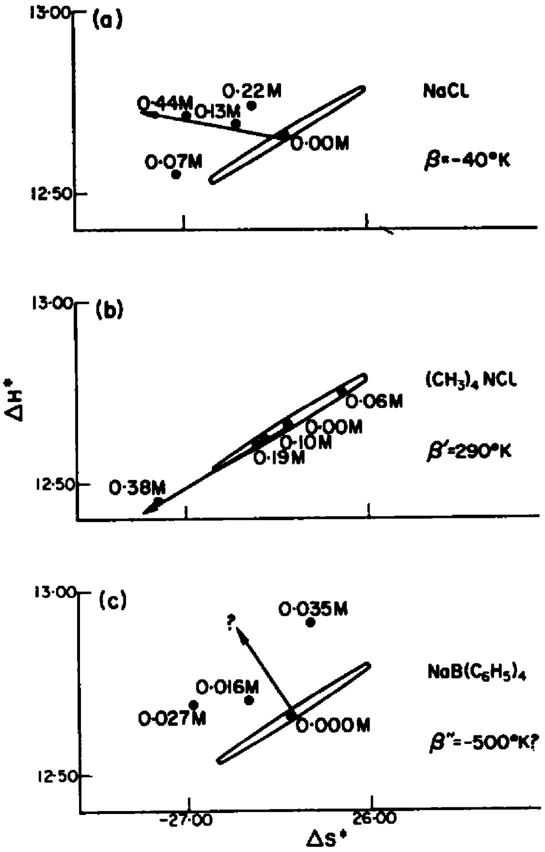

Fig. 1. Salt effects on activation parameters for the alkaline hydrolysis of methyl-1-naphthoate in 50·0 wt. % dioxan-water at 25°. The number next to each experimental point denotes the salt conc. Added salt is (a) NaCl; (b) $(CH_3)_4NCl$; (c) $NaB(C_6H_5)_4$.

The activation parameters obtained with increasing $(CH_3)_4NCl$ concentration seem to define a straight line with a quite different slope, β', of about $+290°$ K. The activation parameters obtained with increasing $NaB(C_6H_5)_4$ concentration probably do not define a straight line; but if we insist on fitting a straight line, the slope, β'', would be about $-500°$ K.

DISCUSSION

According to the data in Table 3-1, the "normal" kinetic salt effect on reaction (1) due to simple inorganic salts is small, negative and approximately colligative. By contrast, the effect of organic-ion salts is highly specific, depending (i) on ionic charge, and (ii) on the structure of the ion (Table 3-2, 3). In order to develop a theory of this effect, it is helpful to consider first the kinetic effect produced by added nonelectrolytes.

Hydrocarbons or aromatic nonelectrolytes produce kinetic effects on reaction (1) that are negative, specific, and—for some structures—quite large. The theory that these effects result from the decrease in the *macroscopic* static dielectric constant that attends the addition of the nonelectrolyte can be rejected at once, because dioxan, which produces a similar decrease (per mole) in the dielectric constant, produces only a very small kinetic effect. In our opinion, these effects result mainly from interactions similar to those that cause micelle formation. We envisage a sorting of molecules on the microscopic level such that the probability of finding a hydrocarbon or aromatic molecule adjacent to a molecule of methyl-1-naphthoate is significantly greater than the corresponding mole-fraction. As a consequence, the microscopic environment of many ester molecules becomes quite nonpolar, and attack by hydroxide ion on such molecules from the bulk is impeded because ionic charge must now be transferred to a lower effective dielectric constant. This theory can therefore explain the marked decrease of k_2.

When the added hydrocarbon or aromatic molecule bears an electric charge, i.e. when it is an organic ion, we believe that the same kind of sorting will persist. If the charge on the organic ion adjacent to the ester molecule is negative, attack by hydroxide ion is repelled electrostatically. The theory, therefore, explains the marked negative salt effect of organic anions. If the charge is positive, attack by hydroxide ion is facilitated electrostatically, and this interaction seems, in most of the cases investigated, to overcome the reduction in rate that would otherwise be expected. The theory, therefore, explains the salt effect of organic cations, which ranges from barely negative to positive.

What we are saying, in effect, is that in a medium that contains a large excess of water molecules, organic ions nevertheless are solvated preferentially by hydrocarbon or aromatic molecules. Our theory, therefore, de-emphasizes the well-known model of a charge in a dielectric continuum of variable water content, according to which an ion is solvated preferentially by water molecules because such solvation produces an increase in the local dielectric constant near the ion.[12,13] Instead, our theory emphasizes interactions of short range, particularly those that involve adjacent molecules. In this approach, the composition of the first solvation shell of an ion is determined primarily by an equilibrium of pairwise interactions. A relevant example is Eq. (4), where the organic ion (Org^+) can have for its neighbour either an ester molecule (Ester) or a solvent molecule (S).

$$\text{Org}^+\cdot\text{Ester} + \text{S}\cdot\text{S} \rightleftharpoons \text{Org}^+\cdot\text{S} + \text{Ester}\cdot\text{S} \tag{4}$$

In order to predict the equilibrium in Eq. (4), we are not allowed to consider only the relative stability of the $\text{Org}^+\cdot\text{S}$ and $\text{Org}^+\cdot\text{Ester}$ molecular pairs; we must consider also the relative stability of the Ester·S and S·S molecular pairs. Thus the equilibrium in (4) can lie on the left even when the pairwise interaction energy of $\text{Org}^+\cdot\text{S}$ is lower (more negative) than that of $\text{Org}^+\cdot\text{Ester}$ (that is, even when $\text{Org}^+\cdot\text{S}$ is intrinsically more stable than $\text{Org}^+\cdot\text{Ester}$) if S·S is sufficiently more stable than Ester·S.

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[12] P. Debye, *Z. Physik. Chem.* **130**, 56 (1927).

[13] G. Scatchard, *J. Chem. Phys.* **9**, 34 (1941).

In considering the salt effects on reaction (1), it is not unreasonable to suppose, on the basis of Van der Waals' interactions of the London dispersion type,[14,15] that an Org^+·(methyl-1-naphthoate) pair might actually be more stable than an $Org^+ \cdot H_2O$ pair. In the methyl-1-naphthoate molecules, some of the virtual electronic oscillators that one envisages in the theory of the dispersion effect[14] have relatively low excitation energies, as indicated by intense optical absorption in the UV above 200 mμ and by an exalted molar refraction. We may suppose, therefore, that these molecules are strong centres of Van der Waals' attraction. On the other hand, the water molecules, because of their small size and low density of electronic oscillators, are notably poor centres of Van der Waals' attraction,[15] yet have a strong tendency towards self-association by means of hydrogen bonds. Thus, in Eq. (4), the pairs Org^+·Ester and S·S are relatively stable, while the pairs Ester·S and, to a lesser extent because of considerations of local dielectric constant, the pairs Org^+·S are relatively unstable. It is difficult to quantify these remarks in the present case, but it is clear from previous work on other systems[15] that differences in pairwise London dispersion energies can amount to as much as several kilocalories.

The hypothesis that there is preferential sorting of hydrocarbon like molecules or ions around nonpolar substrates in water and other hydroxylic solvents is consistent with many additional facts. Let us cite a few examples. Organic-ion salts cause salting-in of nonelectrolytes not only in water[16] but also in 50% dioxan–water.[4] Self-interaction coefficients of nonpolar or slightly polar substrates are quite negative even in 50% dioxan–water.[17] Nonelectrolytes are solubilized by detergent salts in water.[18] Activity coefficients in 50% dioxan–water indicate rather strong attractive interactions between 1-naphthoate ion and 2-naphthalenesulphonate ion in spite of the electrostatic repulsion of the negative charges.[19] Addition of benzene to solutions of $(n\text{–}C_4H_9)_4NBr$ in methanol causes increased ionic dissociation,[20] as if the benzene molecules were forming a stable complex with the organic cations. Quaternary ammonium hydroxides are more effective than potassium hydroxide in catalysing the decomposition of diacetone alcohol in water, and the neutral salt effect of $(C_2H_5)_4NI$ on this reaction is positive while that of KI is negative.[21]

EXPERIMENTAL

Materials. Sodium perchlorate ("chemically pure") was recrystallized from aqueous dioxan; the crystals contained dioxan of crystallization, which was removed by drying for 8 hr in a vacuum oven at 85°. Tetramethylammonium chloride (Eastman white label) was dried to constant weight at 130° before use. The dry salt was neutral and had an equiv. wt. of 109·5 (by chloride titration); cal. for $(CH_3)_4NCl$, 109·6. Sodium nitrate (reagent grade) was recrystallized twice from doubly distilled water and dried thoroughly *in vacuo*. Sodium 2-naphthalenesulphonate was prepared by dissolving 12·3 g sodium acetate trihydrate and 20·6 g 2-naphthalenesulphonic acid in a minimum amount of

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[14] F. London, *J. Phys. Chem.* **46**, 305 (1942); F. London, *Z. Physik. Chem., Leipzig*, **B11**, 222 (1930).

[15] E. Grunwald and E. Price, *J. Amer. Chem. Soc.* **86**, 4517 (1964).

[16] F. A. Long and W. F. McDevit, *Chem. Rev.* **51**, 119 (1952); R. L. Bergen and F. A. Long, *J. Phys. Chem.* **60**, 1131 (1956).

[17] E. Grunwald and G. Baughman, *J. Phys. Chem.* **64**, 933 (1960); W. J. Miller and E. Grunwald, *Ibid.* **68**, 1285 (1964).

[18] M. E. L. McBain and E. Hutchinson, *Solubilization.* Academic Press, New York (1955).

[19] A. F. Butler and E. Grunwald, *J. Phys. Chem.* **67**, 2330 (1963).

[20] R. C. Miller and R. M. Fuoss, *J. Amer. Chem. Soc.* **75**, 3076 (1953).

[21] E. S. Halberstadt and J. E. Prue, *J. Chem. Soc.* 2234 (1952).

hot water. EtOH was added to the hot solution and the salt crystallized by cooling in ice. The product was decolourized twice with charcoal, recrystallized from EtOH–water, washed with EtOH, and dried *in vacuo* over anhydrous magnesium perchlorate. (Found: C, 52·05; H, 3·25, calc. for $C_{10}H_7SO_3Na$: C, 52·17; H, 3·07%.)

Water was doubly distilled from alkaline $KMnO_4$. The purification of *p*-dioxan and the preparation of 50·0 wt. % dioxan–water mixtures followed previous practice.[8] Pure dioxan was stored in the dark under N_2; dioxan–water mixtures were prepared from pure dioxan, which had been distilled not more than 24 hr before. The dioxan–water mixtures which were used in the kinetic experiments were never older than 8 days. Sodium hydroxide (reagent grade) was dissolved in as little water as possible; the concentrated solution (18 N) was filtered through a glass filter under CO_2-free air, stored in a well-closed polyethylene bottle, and diluted with CO_2-free doubly distilled water as required.

Methyl 1-naphthoate was prepared from 1-naphthoic acid and MeOH according to the method of Clinton and Laskowski.[22] The product was purified by two vacuum distillations; b.p. 159–160° (10 mm); equiv. wt. (by quantitative saponification) 185·4 (calc. 186·2); n_D^{25} 1·6108. The b.p. is in reasonable agreement with a previously reported value.[23]

KBr was recrystallized twice from doubly distilled water. Before use the crystals were ground and dried at 120°. KI was recrystallized from doubly distilled water under N_2. The crystals were washed with EtOH and dried at 120° before use. 2-Naphthyltrimethylammonium chloride was prepared as follows: The iodide was prepared according to Morgan[24] by heating a mixture of 2-naphthylamine, NaOH and MeI in a sealed tube at 120°. An anion exchange resin (DOWEX-1) was used to convert the iodide into the chloride; 12 g of the iodide was dissolved in a mixture of 450 ml MeOH and 350 ml water; this solution was allowed to run through a column (1·6 × 60 cm) filled with the chloride form of the anion exchange resin. The eluate was filtered, and solvent was distilled off under red. press. to give 6·6 g crude 2-naphthyltrimethylammonium chloride. This was dissolved in 17 ml absolute EtOH, treated with charcoal, and reprecipitated by adding 360 ml anhydrous ether, m.p. 175–176·5°; equiv. wt. (by Volhard titration for chloride), 220·3 (calc. for $C_{13}H_{16}NCl$: 221·7).

Phenyltrimethylammonium chloride (Eastman white label) was purified further because the material had a greenish colour and gave a slightly acid aqueous solution, indicating the presence of amine hydrochlorides. A solution of 10 g salt in 35 ml 0·01 M $Ba(OH)_2$ was shaken with 3 portions of chloroform to remove the amines. The aqueous layer was made slightly acid by addition of dil. HCl, and placed in a desiccator over magnesium perchlorate to remove the water. The remaining dry solid material was treated with 45 ml absolute EtOH; norit was added and the solution was allowed to stand for a short while at room temp. After filtration, to separate the norit and $BaCl_2$, a clear solution was obtained. Addition of 200 ml anhydrous ether gave a precipitate, which was allowed to settle overnight. After filtration, the white product gave a neutral aqueous solution in which no Ba ions could be detected. The equiv. wt. (by Volhard titration for chloride) was 171·1 (calc. for $C_9H_{14}NCl$: 171·7).

Tetra-n-butylammonium iodide (Eastman white label) was recrystallized under N_2 from doubly distilled water. Volhard titration for iodide gave an equiv. wt. of 369·5 (calc. for $C_{16}H_{36}NI$: 369·4). The solution of the purified iodide was neutral. Sodium *p*-bromobenzenesulphonate (Eastman white label) was purified because a solution of the salt was acidic, presumably due to the presence of free benzenesulphonic acid. To the solution of 20 g salt in 60 ml doubly distilled water was added 10 g sodium acetate trihydrate and some norit. The solution was heated and then filtered; cooling of the filtrate gave white blades which still gave a slightly acidic solution in water. After dissolving 15 g of these blades in 30 ml hot doubly distilled water and adding 70 ml EtOH, a pure salt, free from acid, was obtained.

Sodium-1-naphthoate could not be isolated as a pure solid from a mixture of 1-naphthoic acid and NaOH. The salt was therefore prepared directly in solution from the pure acid, standard NaOH, dioxan and water so as to give a solution of the neutral salt in 50% dioxan–water.

Two different samples of sodium tetraphenylboride were used. A sample obtained from Baker Chemical Co. gave a slightly alkaline solution in water, and attempts to purify the salt were not successful. When this salt was used in a kinetic experiment, the extra base added with the salt was

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[22] R. O. Clinton and S. C. Laskowski, *J. Amer. Chem. Soc.* **70**, 3135 (1948).

[23] P. Fitzgerald, J. Packer, J. Vaughan and A. F. Wilson, *J. Chem. Soc.* 170 (1956).

[24] G. T. Morgan, *J. Chem. Soc.* 822 (1900).

taken into account. A sample obtained from Fa. Heyl and Co., Germany, gave a neutral aqueous solution and was used without further purification.

Stability of the salts under reaction conditions. Although tetraphenylboride ion is decomposed by acid, the extent of decomposition was found to be negligible under the conditions of the acid-base titrations used in the analysis of the reaction mixtures. All other salts were found to be stable under the reaction conditions.

Rate measurements and calculations. The alkaline hydrolysis of methyl 1-naphthoate was carried out in 100 ml volumetric flasks. The necks of these flasks were graduated in 0·1 ml increments from 100 to 110 ml. After introduction of accurately weighed amounts of the ester and of neutral salt, solvent was added up to a total volume of about 90 ml, the mixture was shaken to produce a homogeneous solution, and brought to the desired temp (±0·05°) in a constant-temperature bath. The desired amount of 0·1 N NaOH in 50 wt. % dioxan–water was then added from a burette, and additional dioxan–water was added, as needed, to produce a final volume of reaction mixture between 100 and 110 ml. The exact volume was read with the help of the graduation marks on the neck of the volumetric flask after temp equilibrium was re-established. Five-ml samples of the reaction mixture were withdrawn from the flask at suitable intervals, reaction was quenched by adding a known excess of standard 0·01 N HCl, and the mixtures were analysed by acid-base titration of the excess acid with 0·01 N NaOH, using a calibrated 5-ml microburette and cresol red (3 drops of 0·04% solution in EtOH) as the endpoint indicator. These titrations were carried out under N_2 in order to exclude CO_2 from the air. The endpoints of the titrations were usually quite sharp, and the required amount of base could be determined to 0·005 ml. The first two samples were taken with an interval of 2 minutes; the average sampling time was taken as zero time and the average NaOH concentration as the NaOH concentration at zero time. In most runs, 5 other samples were taken at later times so as to follow the reaction for approximately two half-lives.

Reaction (1) was found to follow good second-order kinetics in all experiments. Second-order rate constants, k_2 or k_2°, were calculated from the data for each run by standard least squares statistical methods.[25]

Spectral measurements. The optical densities used for the calculation of the extinction coefficients in Table 5 were measured with a recording Beckman spectrophotometer (model DK). Before use the quartz cells were soaked in conc. HNO_3 and subsequently rinsed with water, dil. ammonia, water and EtOH; the cells were dried in a vacuum desiccator. The 0·1-mm cells were rinsed several times with the solution before use, and special care was taken to avoid air bubbles in the light path. The reference cell was always filled with 50 wt. % dioxan–water.

[25] For details, see E. F. J. Duynstee, *Kinetic Salt Effects in Dioxan–Water.* Academisch Proefschrift, Universiteit van Amsterdam (1959).