Mechanistic Studies in Strongly Basic Media. Part II.[1] Indicator Equilibria in t-Butyl Alcohol

By D. Bethell and A. F. Cockerill

The relative acidities of a number of primary aromatic amine indicators in t-butyl alcohol containing sodium and potassium t-butoxides or benzyltrimethylammonium hydroxide have been determined. An empirical measure of the basicity of solutions of sodium and potassium t-butoxides in t-butyl alcohol has been defined. The basicity of such solutions decreases with increasing temperature but is increased substantially by addition of dimethyl sulphoxide, tetrahydrothiophen *SS*-dioxide, or pyridine *N*-oxide.

IN Part I [1] the extent of conversion of 4-nitroaniline into its conjugate base was used as an empirical measure of the basicity of solutions of benzyltrimethylammonium hydroxide and potassium t-butoxide in t-butyl alcohol in order to correlate rates of conversion of 9-bromofluorene to bifluorenylidene. We now report an investigation of the ionisation of other primary aromatic amine indicators, undertaken in connection with more extensive mechanistic investigations.

EXPERIMENTAL

All solutions were stored and handled in a dry box maintained at 30° ± 1°.

Materials.—*Solvents.* t-Butyl alcohol, purified as previously described,[1] had m. p. 25·5°. Dimethyl sulphoxide, twice distilled under reduced pressure from calcium hydride, had m. p. 18·4°. Tetrahydrothiophen *SS*-dioxide, processed similarly, had m. p. 28°. Pyridine *N*-oxide, fractioned twice under reduced pressure, had m. p. 67°.

Bases. Solutions of potassium t-butoxide in t-butyl alcohol were usually prepared directly from the metal as described previously. In some experiments, however, the potassium salt was isolated, sublimed, and dissolved in t-butyl alcohol. Fresh solutions prepared by these two procedures were indistinguishable. Solutions of sodium t-butoxide were prepared similarly. Benzyltrimethylammonium hydroxide was a commercial aqueous solution. Solutions of benzyltrimethylammonium t-butoxide in t-butyl alcohol were prepared by mixing equivalent quantities of potassium t-butoxide and benzyltrimethylammonium chloride with removal of the precipitated potassium chloride by centrifuging. Such solutions darken on prolonged storage, so were used as soon as possible after preparation.

Indicators. Commercial specimens were purified by column chromatography and recrystallisation. Their m. p.s agreed with literature values. The aminoazobenzenes were prepared by coupling the appropriately substituted diazonium salt with aniline. With the exceptions noted below all, on contact with base, showed instantaneous colour changes which could be reversed by neutralisation. The colour in the presence of base, assumed to be that of the indicator conjugate base, remained stable for at least 30 min.

Indicator Measurements.—Unless stated otherwise, these were carried out at 30·0°. The ionisation ratio $R = [\mathrm{ArNH^-}]/[\mathrm{ArNH_2}]$ was determined from spectrophotometric measurements at the wavelength of maximum absorption of the indicator conjugate base, ArNH$^-$, by use of the equation $R = (\varepsilon_{\mathrm{obs}} - \varepsilon_{\mathrm{A}})/(\varepsilon_{\mathrm{B}} - \varepsilon_{\mathrm{obs}})$. Here ε_{A} is the extinction coefficient of ArNH$_2$, ε_{B} that for ArNH$^-$, and $\varepsilon_{\mathrm{obs}} = D_{\mathrm{obs}}/([\mathrm{ArNH_2}] + [\mathrm{ArNH^-}])$, D_{obs} being the observed optical density (1 cm. cell) of the basic solution in question. Indicators were used only in media for which $0{\cdot}1 < R < 10$: outside these limits reproducibility was poor. Values of ε_{B} were obtained by progressive increase in base concentration until no further increase in $\varepsilon_{\mathrm{obs}}$ occurred. Using 4-(4-nitrophenylazo)aniline in solutions of potassium t-butoxide in t-butyl alcohol, $\varepsilon_{\mathrm{obs}}$ passed through a maximum at high base concentration. In this case the value of ε_{B} appropriate to media in which the indicator was only partly ionised was estimated by extrapolation to $[\mathrm{KOBu}]^{-1} = 0$ of the linear portion of a graph of $\varepsilon_{\mathrm{obs}}{}^{-1}$ against $[\mathrm{KOBu}]^{-1}$.[2] In the temperature range 30—50°, the variation in ε_{A} and ε_{B} for 4-chloro-2-nitroaniline was negligible. Results are in Tables 3 and 4.

As with 4-nitroaniline, spectra characteristics of the conjugate bases of the indicators varied according to the nature of the counter-ion. Changes in $\lambda_{\mathrm{max.}}$ were, however, much less than for 4-nitroaniline (Table 1). Addition of dimethyl sulphoxide, tetrahydrothiophen *SS*-dioxide, or pyridine *N*-oxide to indicator solutions containing potassium t-butoxide generally altered $\lambda_{\mathrm{max.}}$ and $\varepsilon_{\mathrm{B}}{}^{\mathrm{max.}}$ in the direction of those observed with benzyltrimethylammonium hydroxide, the transformation usually being complete when the additive was at a concentration of about 1M. At all additive concentrations, ε_{B}, determined at high base concentration, was found to be independent of the base concentration, even in the case of 4-(4-nitrophenylazo)aniline. 4-Nitroaniline was exceptional, however: $\lambda_{\mathrm{max.}}$ and $\varepsilon_{\mathrm{B}}{}^{\mathrm{max.}}$ were both greater in the presence of dimethyl sulphoxide–potassium t-butoxide than when benzyltrimethylammonium hydroxide was the base, and ε_{B} varied

TABLE 1

Spectral constants of indicators and their conjugate bases in t-butyl alcohol at 30° *

	Cation								
	$\mathrm{PhCH_2N^+Me_3}$			K^+			$\mathrm{Na^+}$		
Indicator	$\lambda_{\mathrm{B}}{}^{\mathrm{max.}}$	$\varepsilon_{\mathrm{B}}{}^{\mathrm{max.}}$	ε_{A}	$\lambda_{\mathrm{B}}{}^{\mathrm{max.}}$	$\varepsilon_{\mathrm{B}}{}^{\mathrm{max.}}$	ε_{A}	$\lambda_{\mathrm{B}}{}^{\mathrm{max.}}$	$\varepsilon_{\mathrm{B}}{}^{\mathrm{max.}}$	ε_{A}
I	470	35,700	0	468	32,600	0	468	32,600	0
II	463	32,700	0	458	30,100	0	—	—	—
III	490	8640	215	488	7870	255	488	7870	255
IV	—	—	—	432	25,100	1250	—	—	—
V	462	28,200	0	432	25,300	1460	—	—	—
VI	—	—	—	468	6970	1840	—	—	—
VII	—	—	—	620	34,500	0	—	—	—

* $\lambda_{\mathrm{B}}{}^{\mathrm{max.}}$ in mμ; ε_{A} recorded at $\lambda_{\mathrm{B}}{}^{\mathrm{max.}}$.

Indicators: I, 2,6-dichloro-4-nitroaniline; II, 2,5-dichloro-4-nitroaniline; III, 4-chloro-2-nitroaniline; IV, 2-methyl-4-nitroaniline; V, 4-nitroaniline; VI, 4-methyl-2-nitroaniline; VII, 4-(4-nitrophenylazo)aniline.

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[1] D. Bethell, *J. Chem. Soc.*, 1963, 666 is considered as Part I.

[2] C. Jacquinot-Vermesse, R. Schaal, and P. Souchay, *Bull. Soc. Chim. France*, 1960, 141.

somewhat with base concentration. This indicator was therefore not used in studies on mixed solvents.

TABLE 2

Spectral constants of indicator conjugate bases in t-butyl alcohol containing potassium t-butoxide and added solvents at 30°

Indicator		I	III	V	VII
$\lambda_B^{max.}$		470	490	460	620
Dimethyl sulphoxide	0·21M	—	8150	—	41,800
	0·43M	—	8370	—	45,300
	0·65M	—	8510	—	47,400
	1·0M	35,700	8730	28,100 *	48,500
Tetrahydrothiophen *SS*-dioxide	1M	35,700	—	—	49,100
Pyridine *N*-oxide	1M	35,700	9000	—	49,100

* 32,000 at 466 mμ in the presence of 3M-additive (cf. ref. 4).

TABLE 3

Indicator ionisation ratios (R) in solution of potassium t-butoxide in t-butyl alcohol at 30° *

Indicator I								
10^4[KOBu] (M)	1·84	3·06	3·72	4·17	4·87	5·98	6·12	12·9
R................	0·95	2·16	2·59	3·24	3·97	5·29	4·60	9·84
Indicator II								
10^4[KOBu] (M)	1·43	2·16	2·59	4·31	5·18	5·62	5·88	8·51
R................	0·15	0·44	0·56	1·32	1·83	1·86	1·77	2·56
10^4[KOBu] (M)	10·4	12·9						
R................	4·51	6·04						
Indicator III								
10^4[KOBu] (M)	4·5	5·6	6·4	10·0	12·7	15·0	20·0	
R................	0·10	0·13	0·15	0·24	0·32	0·38	0·50	
10^4[KOBu] (M)	25·4	30·5	46·8	52·2	62·4	79·8	104	
R................	0·69	0·85	1·01	1·45	1·67	2·43	3·61	
10^4[KOBu] (M)	171	237						
R................	5·26	8·48						
Indicator IV								
10^4[KOBu] (M)	9·27	186	190	380	756			
R................	0·84	1·78	1·65	4·05	9·59			
Indicator V								
10^4[KOBu] (M)	21·0	41·0	66·0	145	400	660	955	
R................	0·10	0·23	0·33	0·65	4·00	4·32	6·02	
Indicator VI								
10^4[KOBu] (M)	95·0	167	257	370	623	1490		
R................	0·26	0·46	0·89	1·33	2·66	8·43		
Indicator VII								
10^4[KOBu] (M)	43·9	84·0	137	191	318	477	549	
R................	0·22	0·29	0·54	0·59	0·91	1·21	1·51	
10^4[KOBu] (M)	637	1110	1280	1370				
R................	1·88	3·21	3·06	4·22				

* Nominal indicator concentrations were ~10^{-5}M throughout.

In addition to the indicators listed in Table 1, the following were examined with a view to use for solutions of potassium t-butoxide in t-butyl alcohol more concentrated than 0·1M, but were rejected: *N*-methyl-4-nitroaniline (reacted irreversibly with the medium); 3-nitroaniline, 4-cyanoaniline, and 4-phenylazoaniline (no colour change in 0·9M-potassium t-butoxide in t-butyl alcohol); 2-methoxy-4-nitroaniline (fully ionised in 0·01M-potassium t-butoxide in t-butyl alcohol); 4-methoxy-2-nitroaniline (spectra of indicator and conjugate base overlap seriously).

TABLE 4

Indicator ionisation ratios (R) in solutions of sodium t-butoxide in t-butyl alcohol at 30°

Indicator I								
10^4[NaOBu] (M)	5·18	5·26	6·05	6·91	8·77	15·1	17·5	35·1
R................	1·86	1·90	2·11	2·63	3·54	7·00	8·20	(15·2)
Indicator III								
10^4[NaOBu] (M)	17·3	31·5	34·6	94·4	157	315	629	
R................	0·20	0·41	0·47	1·40	2·95	7·14	(14·1)	

RESULTS AND DISCUSSION

Evaluation of pK_a *Values.*—The indicator equilibrium in t-butyl alcohol containing alkali-metal t-butoxides may be represented:

$$\mathrm{ArNH_2 + M^+OBu^- \rightleftharpoons ArNH^-M^+ + (}m\mathrm{ + 1)BuOH}$$

where m represents the difference in solvation number between $\mathrm{ArNH_2 + M^+OBu^-}$ and $\mathrm{ArNH^-M^+}$. The corresponding equilibrium constant is given by:

$$K_b^{\mathrm{BuOH}} = \frac{(\mathrm{ArNH_2})(\mathrm{M^+OBu^-})}{(\mathrm{ArNH^-M^+})(\mathrm{BuOH})^{(m+1)}}$$

whence

$$\mathrm{p}K_b^{\mathrm{BuOH}} = \log R - \log[\mathrm{M^+OBu^-}] + (m + 1) \log (\mathrm{BuOH}) + \log(f_\mathrm{B}/f_\mathrm{A}f_\mathrm{MOBu}) \quad (1)$$

Here, square brackets denote concentrations, parentheses activities; f is an appropriate activity coefficient, the subscripts A and B referring to $\mathrm{ArNH_2}$ and $\mathrm{ArNH^-M^+}$, respectively. Pure t-butyl alcohol being taken as the reference state, in infinitely dilute solution, the last two terms in equation (1) vanish: pK_b^{BuOH} should thus be capable of evaluation provided that accurate extrapolation of log R — log [$\mathrm{M^+OBu^-}$] is possible.[3] Over the range of base concentrations studied (log R — log [$\mathrm{M^+OBu^-}$]) showed little variation, but extrapolation to [$\mathrm{M^+OBu^-}$] = 0 gave lower values of pK_b^{BuOH} for 2,6-dichloro-4-nitroaniline and 4-chloro-2-nitroaniline when M was changed from potassium to sodium. Clearly our extrapolation is inaccurate, even in these dilute solutions.

We have therefore adopted an alternative approach.[4] Any pair of indicators being designated by the subscripts 1 and 2, at a given concentration of base,

$$\mathrm{p}K_{b1}^{\mathrm{BuOH}} - \mathrm{p}K_{b2}^{\mathrm{BuOH}} = \log R_1 - \log R_2 + \log(f_{\mathrm{B}1}f_{\mathrm{A}2}/f_{\mathrm{A}1}f_{\mathrm{B}2})$$

From the conventional assumption that, for indicators of similar structure, activity-coefficient ratios of the type $f_\mathrm{A}/f_\mathrm{B}$ are independent of the indicator at a given medium composition,

$$\mathrm{p}K_{b1}^{\mathrm{BuOH}} - \mathrm{p}K_{b2}^{\mathrm{BuOH}} = \mathrm{p}K_{a2}^{\mathrm{BuOH}} - \mathrm{p}K_{a1}^{\mathrm{BuOH}} = \log R_1 - \log R_2$$

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[3] R. A. More O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 1963, 5030, 5035.

[4] (*a*) R. Stewart and J. P. O'Donnell, *J. Amer. Chem. Soc.*, 1962, **84**, 493; (*b*) R. Stewart and J. P. O'Donnell, *Canad. J. Chem.*, 1964, **42**, 1681.

Graphs of log R against log$[M^+OBu^-]$ were approximately linear as required by equation (1) if the last two terms are effectively constant. The slopes were somewhat higher than theoretical, being in the range 1·35 to 1·05, and apparently decreased as the indicator became less acidic and the base concentration required to effect measureable ionisation increased.* Because of this variation in slope, Δ log R was read from the graphs at the base concentration at which $\log R_1 + \log R_2 = 0$. Values of ΔpK_a^{BuOH} for the indicators relative to 4-chloro-2-nitroaniline are given in Table 6.

TABLE 5

Determination of ΔpK_a^{BuOH} ($= \log R_{II} - \log R_{III}$) for 2,5-dichloro-4-nitroaniline (II) and 4-chloro-2-nitroaniline (III) in t-butyl alcohol containing benzyltrimethylammonium hydroxide and water at 30°

Solution	R_{II}	R_{III}	ΔpK_a^{BuOH}
1	2·24	$0{\cdot}22_3$	1·00
2	9·28	0·68	1·13
3	3·77	$0{\cdot}24_7$	1·17
4	2·67	$0{\cdot}27_1$	0·99
5	8·59	0·67	1·11
6	3·52	0·39	0·96
7	5·56	0·55	1·01
8	3·04	$0{\cdot}27_9$	1·04
9	9·65	$0{\cdot}11_2$	0·94
			Average 1·04 ± 0·08

TABLE 6

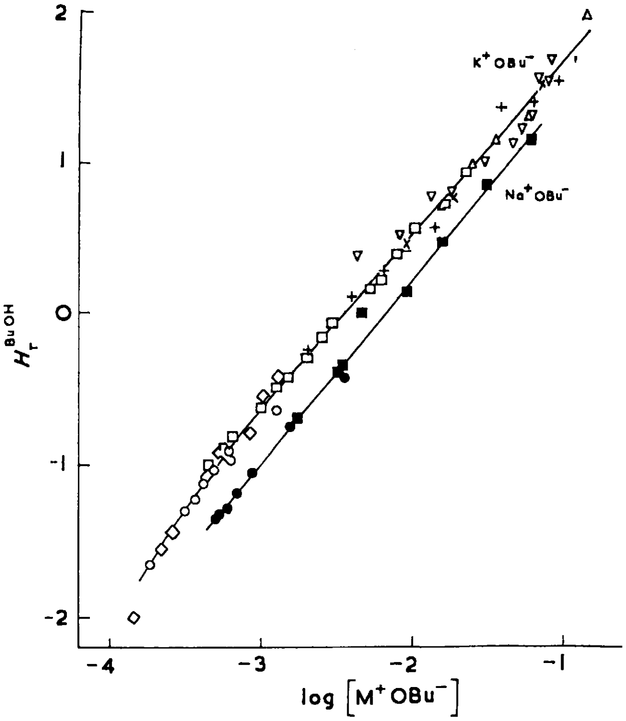
ΔpK_a^{BuOH} values for indicators in t-butyl alcohol containing various bases at 30°

Indicator	K^+OBu^-	Na^+OBu^-	$PhCH_2N^+Me_3\ O^-H$	Lit.*
I	−1·63	−1·60	−1·56	−1·67
II	−1·19	—	−1·04	−1·17
III	0·00	0·00	0·00	0·00
IV	0·54	—	—	—
V	0·75	—	1·04	1·15
VI	1·03	—	—	—
VII	1·04	—	—	—

* Ref. 3: quaternary ammonium hydroxide in a variety of aqueous organic solvents.

A slightly different procedure was adopted for evaluating ΔpK_a^{BuOH} values in solutions of benzyltrimethylammonium hydroxide in slightly aqueous t-butyl alcohol. It was shown[1] that in such solutions $R \propto [PhCH_2NMe_3^+OH^-]/[H_2O]$ [2] for 4-nitroaniline and, since, in the present investigation, the base and water concentrations were quite low, a method analogous to that for solutions of alkali t-butoxides would have been lengthy and of low accuracy. Instead, pairs of indicators (I—II, II—III, III—V) were compared directly by determination of R for each indicator in portions of the same solution of the base in aqueous t-butyl alcohol. Values of Δ log R were determined for each solution, about ten different solutions covering a range of base and water concentrations being used for each pair of indicators. One such determination is detailed in Table 5 and ΔpK_a^{BuOH} values are given in Table 6. Standard deviations of Δ log R were about 10% of the recorded value, indicating the generality of the proportionality of R to $[PhCH_2NMe_3^-OH^-]/[H_2O]$ [2] in these media.

In Table 6, values of ΔpK_a^{BuOH} are compared with values reported by Stewart and O'Donnell[4] for the same indicators in aqueous tetramethylenesulphone, pyridine, etc., referred to the standard state of pure water. For the more acidic indicators agreement is within the combined uncertainties of the measurements. In the case of 4-nitroaniline, ΔpK_a^{BuOH} derived from measurements using potassium t-butoxide as base is substantially lower than the value, obtained from experiments in slightly aqueous t-butyl alcohol containing benzyltrimethylammonium hydroxide, which accords with that of Stewart and O'Donnell. Similar discrepancies occur in t-pentyl alcohol.[5]



Acidity function H_r^{BuOH} for sodium and potassium t-butoxides in t-butyl alcohol at 30°. Indicators I (○), II (◇), III (□), IV (×), V (+), VI (△), and VII (▽)

The Basicity of Solutions of Alkali t-Butoxides in t-Butyl Alcohol.—Using the values of R (Tables 3 and 4) and ΔpK_a^{BuOH} (Table 6), we can define an acidity function (H_r^{BuOH}) by the equation, $H_r^{BuOH} \equiv \Delta pK_a^{BuOH} + \log R$. It is evident that $H_r^{BuOH} = 0$ for solutions in which 4-chloro-2-nitroaniline is half-ionised. Clearly this function lacks the rigour of the Hammett function H_-, but serves as an empirical measure of the basicity of solutions of alkali t-butoxides in t-butyl alcohol which is useful in the correlation of kinetic data for such media. The relationship between H_r^{BuOH} and log $[M^+OBu^-]$ is show in the Figure for sodium and potassium t-butoxides up to concentrations of about 0·1M.

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* 4-Methyl-2-nitroaniline seems anomalous, but results are least accurate for this indicator because of the relatively high value of ε_A at $\lambda_B^{max.}$ (Table 1).

[5] Results of ref. 2 adjusted as in ref. 3*b*; see also C. Vermesse-Jacquinot, *J. Chim. phys.*, 1965, **62**, 198.

It can be seen that solutions of potassium t-butoxide are about twice as basic as solutions of sodium t-butoxide of the same concentration, even when this is very low. Somewhat similar differences in basicity exist in solutions of alkali methoxides in methanol, but these disappear at base concentrations less than 0·2M.[6] With benzyltrimethylammonium t-butoxide in t-butyl alcohol at concentrations as low as 10^{-3}M, even the least acidic indicators appeared to be completely ionised, suggesting that such solutions are at least 1000 times more basic than a solution of potassium t-butoxide of the same concentration. All these observations point to the conclusion that an important factor determining the basicity of solutions of t-butoxides in t-butyl alcohol is the extent to which the base exists in the form of ionic aggregates.

Such association of oppositely charged species is to be expected since t-butyl alcohol is of low polarity (dielectric constant 11·2 at 30°) and there must be appreciable steric hindrance to solvation of cations. Raising the temperature decreases the dielectric constant of t-butyl alcohol to 9·7 at 40° and 8·6 at 50°,[7] and matching this, values of R for 4-chloro-2-nitroaniline ($=H_r^{\text{BuOH}}$) also decrease (Table 7). At a given concentration of potassium t-butoxide, the basicity is roughly halved on raising the temperature from 30° to 50°. This effect will be superimposed on the normal temperature effect on ionisation constants of weak acids which is expected to be small.

TABLE 7

Influence of temperature on R for 4-chloro-2-nitroaniline in t-butyl alcohol containing potassium t-butoxide

Temp.					
30°	10^3[KOBu] (M)	3·69	7·38	11·1	14·8
	R *	0·93	1·99	3·13	4·27
35	10^3[KOBu] (M)	3·69	7·38	—	14·8
	R	0·87	1·80	—	3·73
40	10^3[KOBu] (M)	3·69	7·38	11·1	14·8
	R	0·74	1·59	2·46	3·11
45	10^3[KOBu] (M)	3·19	6·38	12·8	25·5
	R	0·59	1·26	2·30	5·75
50	10^3[KOBu] (M)	3·19	6·38	12·8	25·5
	R	0·57	1·21	2·39	4·98

* Values interpolated from results of Table 3.

The effect of added dimethyl sulphoxide, tetrahydrothiophen *SS*-dioxide, and pyridine *N*-oxide on R for 4-(4-nitrophenylazo)aniline at a fixed concentration of potassium t-butoxide is given in Table 8. All three additives increased R, but, in the range of concentrations examined (up to 2M) tetrahydrothiophen *SS*-dioxide was by far the most effective. The influence of the sulphur-containing additives in t-butyl alcohol is similar to that observed at comparable additive concentrations in other hydroxylic solvents.[4,8] A number of factors may contribute to the enhancement of basicity in t-butyl alcohol, *e.g.*, increase in dielectric constant, equilibrium between t-butoxide ion and the conjugate base of the additive,[9] specific solvation effects, their relative importance depending on the additive.

TABLE 8

Influence of added substances on the ionisation ratio (R) for 4-(4-nitrophenylazo)aniline in t-butyl alcohol containing 0·0163M-potassium t-butoxide at 30°

Additive	Concn. (M)	R	H_r^{BuOH}
—	—	0·47	0·71
$(CH_2)_4SO_2$	0·102	0·79	0·94
	0·204	1·25	1·14
	0·305	1·65	1·26
	0·509	2·50	1·44
	0·611	3·53	1·59
	0·713	4·63	1·71
	0·814	5·08	1·75
$(CH_3)_2SO$	0·217	0·47	0·71
	0·433	0·53	0·77
	0·650	0·62	0·83
	0·975	0·83	0·96
	1·30	1·08	1·07
	1·73	1·60	1·24
	2·17	2·35	1·41
C_5H_5NO	0·409	0·84	0·96
	0·572	0·81	0·95
	0·818	0·83	0·96
	1·23	0·99	1·03
	1·70	1·41	1·19

Because of their effect on the spectral characteristics of the indicator conjugate bases, it seems that, in the present study, the additives increase the basicity of the media partly by promoting the dissociation of ionic aggregates. In addition, the pronounced cooling which accompanies mixing of these additives with t-butyl alcohol indicates profound changes in the solvent structure, and these must result in modification to the pattern of solvent–solute interactions. One of the most important of these interactions is the solvation of potassium t-butoxide, since a stable complex with t-butyl alcohol is known in the solid state[10] with the alcohol hydrogen-bonded to the alkoxide oxygen, and this seems likely to persist in solution.

ROBERT ROBINSON LABORATORIES, THE UNIVERSITY,
LIVERPOOL 7.
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