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Anion Solvation Properties of Protic Solvents. 1. Spectroscopic Study

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A spectroscopic index for the polarity of solvents, such as Dimroth and Reichardt's E_T, is also a measure of the solvating ability of these solvents toward anions. Few data for protic solvents, in particular acidic ones, have been reported in the literature. Measurements of E_T have been made with the betaine dye 2,6-diphenyl-4-(2′,4′,6′-triphenyl-1-pyridino)phenoxide for over 40 protic solvents, such as the alcohols from methanol to dodecanol and various substituted phenols, and with the dye 4-(2′,4′,6′-triphenyl-1-pyridino)phenoxide for some 20 of these solvents. For some more acidic solvents, such as carboxylic acids, Kosower's Z values have been determined with 4-cyano-1-ethylpyridinium iodide, and Mayer, Gutmann, and Gerger's AN values with tributylphosphine oxide. The values were intercompared, and the effects of the presence of base (triethylamine) and water on the E_T values have been studied. These indexes have been correlated with structural factors for the alcohols and phenols, and with the acidity of the phenols. These correspondences permit the prediction of E_T and the solvation properties of solvents which have not been studied yet.

Introduction

Solvents for electrolytes are characterized not only by their bulk dielectric constants, but also by their donor and acceptor properties. The former determine their dissociating power for the electrolytes, the latter the solvation of the ion pairs or of the ions produced on dissociation. The cations are Lewis acids, so that their solvation is mainly determined by the donor properties of the solvents, which can be expressed, e.g., by Gutmann's donor numbers[1] DN. The anions, as Lewis bases, are not solvated much by aprotic solvents, even if dipolar. Protic solvents, however, solvate anions well, and their acceptor properties play the major role in this respect.

The (electron pair) acceptor properties of protic solvents measure, inter alia, their ability to form hydrogen bonds. They can be expressed by indices such as Dimroth and Reichardt's[2] E_T, Kosower's[3] Z, or Mayer, Gutmann, and Gerger's[4] AN. These indices are based on spectroscopic observations on indicator compounds dissolved in these solvents, the former two in the ultraviolet-visible range, and the latter of nuclear magnetic resonance chemical shifts. Each index has its advantages and drawbacks, but they are mutually well correlated.[2,4] Solvents which are inaccessible by the one method can be studied by another, so that a unified solvent scale can be set up.

A relation exists between the acceptor properties and the solvating power of the solvents toward anions, i.e., the Gibbs free energy of solvation of the anions, $\Delta G°_{solv}(X^-,S)$, where X^- is the generalized anion and S the solvent. The transfer Gibbs free energy of the anion X^- from water to the solvent S is the accepted measure of the anion solvating power of the solvents S (relative to water).[5–7]

$$\Delta G°^{tr}(X^-,H_2O \rightarrow S) = \Delta G°_{solv}(X^-,S) - \Delta G°_{hydr}(X^-) \quad (1)$$

It is the purpose of this paper to present information on the solvent properties of a fairly large number of protic solvents, in particular alcohols and phenols, in terms of E_T, and to compare the data with information available from other properties. In a subsequent paper,[8] the acceptor properties of the solvents will be compared with the anion-solvating properties, both in terms of $\Delta G°^{tr}$ data from the literature, critically examined, and in terms of a novel extractive procedure to obtain approximate individual transfer Gibbs free energies.[9]

The Dimroth and Reichardt[3] index E_T had been selected because the indicator compound (betaine no. 30, see Experimental Section) used for the construction of this scale has a large solvent sensitivity. The charge transfer band (first low-energy, long-wavelength $\pi \rightarrow \pi^*$ absorption band) ranges from ~ 130 kJ mol^{-1} (925 nm) for hexane to ~ 264 kJ mol^{-1} (453 nm) for water. Combined with the precision attainable, ± 0.5 kJ mol^{-1}, this range yields a very fine resolution of the properties of similar solvents, comparable, e.g., with the Z scale,[3] and does not require a series of measurements with extrapolation to zero concentration of the indicator compound, as does the AN scale.[4] A difficulty with the E_T scale concerning slightly acidic solvents, of which the AN scale is free, has been overcome[10] for the protic solvents of interest in the present connection. This, admittedly, is not the case for carboxylic acid solvents, for which the AN scale seems to be the more practical one available.

Experimental Section

Materials. The solvents were generally of chemically pure grade, except where noted below. Only practical or technical grades of the following solvents were available: 2-chloroaniline, *N*-methylaniline, 2,4-dimethylphenol, 2-*tert*-butyl-5-methylphenol, 2-*sec*-butylphenol, 4-*sec*-butylphenol, 2-*sec*-propylphenol, 2-chlorophenol, nonylphenol, 2-hydroxyethyl salicylate, and trichloroethanol. A further sample of the latter and 4-methoxybenzyl alcohol

were synthesized in the laboratory by reduction of the corresponding aldehydes with sodium borohydride. The solvents were generally distilled once from molecular sieves, and the constant boiling fraction was utilized. The water content of the distillation product was <0.3%.

A sample of 2,6-diphenyl-4-(2′,4′,6′-triphenyl-1-pyridino)phenoxide (betaine dye no. 30 in the list[2a]) was kindly supplied by Professor Reichardt, and a sample of 4-(2′,4′,6′-triphenyl-1-pyridino)phenoxide (betaine dye no. 1 in the list[2a]) was kindly supplied by Professor Rappoport. Transition energies of the former dye will be designated as E_T and those of the latter dye by E_T' (in place of the symbols $E_T(30)$ and $E_T(1)$, respectively, used by other authors[10,11]). The indicator compound 4-cyano-N-ethylpyridinium iodide[3] was synthesized from 4-cyanopyridine and ethyl iodide in acetonitrile, and crystallized by vaporization of the solvent. The indicator compound tributylphosphine oxide (Eastman Kodak) served in lieu of triethylphosphine oxide[4] for the ^{31}P nuclear magnetic resonance measurements.

Procedures. Absorption spectra were measured on a Cary 14 spectrophotometer at room temperature, unless otherwise noted. A small quantity of dye was added to the solvent, and the spectrum of the solution was taken against the solvent as reference. Several of the solvents supercool readily and were measured at room temperature, 23 ± 2°C, even though it was below their freezing points. Where required, the cells were placed in blocks through which heated water from a thermostat was pumped. The temperature had but a small effect on the position of the absorption peak, and minor effect on its height, due to the expansion of the solution on heating.

The transition energies were obtained from the wavelengths λ_{max} for the maximum in the absorption peak for the dye $\pi \rightarrow \pi^*$ transition (long wavelength transition), corrected, where necessary for the sloping background of the higher energy transition, when a relatively high concentration of the dye had to be used. The value of E_T was calculated from

$$E_T/\text{kJ mol}^{-1} = 10^6 h c N_A (\lambda_{max}/\text{nm})^{-1} =$$
$$1.1962 \times 10^5 (\lambda_{max}/\text{nm})^{-1} \quad (2)$$

where h is Planck's constant, c the velocity of light, and N_A Avogadro's number.

Well-resolved absorption peaks were obtained for most solvents with $E_T \leq 220$ kJ mol^{-1}, while with aromatic solvents with $E_T > 220$ kJ mol^{-1} some overlap with the charge transfer band of the solvent occurred. Measurements with varying concentrations of the dye helped somewhat, and a computerized subtraction of the long wavelength absorption edge of the high-energy transition of the dye helped, too. For the more acidic solvents, the addition of a low concentration of base, triethylamine,[10] helped to bring out the $\pi \rightarrow \pi^*$ transition of the betaine dye. The energy resolution of the less acidic solvents, ±0.5 kJ mol^{-1}, is therefore better than that for the more acidic ones, where, e.g., phenol it is not better than ±4 kJ mol^{-1}.

For the substituted ethylpyridinium iodide indicator the procedure was similar to that employed with the betaine dyes. Well-resolved peaks were obtained, and their transition energies were obtained from (2), the symbol Z (for 4-carbomethoxy-) or Z' (for 4-cyano-) being substituted for the symbol E_T.

Nuclear magnetic resonance measurements were made on a Bruker WP-60 Fourier transform NMR instrument. Concentrated (aqueous) phosphoric acid (85%) was used as an external reference. A volume of 0.2 cm^3 of tributylphosphine oxide (1 mmol) was dissolved in a given

TABLE I: Transition Energies in kJ mol^{-1} of the Betaine Dyes in Various Protic Solvents

solvent	E_T	E_T'
Alcohols		
methanol	233.0 (232.0)[a]	277.0
ethanol	217.5 (217.0)	258.0
1-propanol	213.0 (212.0)	250.0
1-butanol	210.5 (210.0)	247.0
1-pentanol	209.0	245.5
1-hexanol	206.5	244.0
1-heptanol	206.5	
1-octanol	203.0	241.5
1-decanol	201.0	
1-dodecanol	199.0	
3-methyl-1-butanol	208.0 (196.5)	
2-ethyl-1-hexanol	193.5	223.5
2-propanol	204.5 (203.5)	
2-octanol	191.0	220.0
benzyl alcohol	214.0 (212.5)	
2-phenylethanol	211.5	
4-methoxybenzyl alcohol	214.0	
2,2,2-trichloroethanol	237.0	
2,2,2-trifluoroethanol	260.0 [271.0][b]	306.5[c]
2,2,3,3-tetrafluoropropanol	(248.5)	
ethanol + n-hexane (equimolar)	203.0	
Phenols		
phenol[d,e]	257	
2-cresol[d]	219.5	
3-cresol	223.5	
4-cresol[e]	254.5	
2-ethylphenol	213.5	
4-ethylphenol[d,e]	256.0	
2,4-xylenol	212.5	
2,6-xylenol[d]	(199.0)[a]	
2-(2-propyl)phenol	209.5	
2-(2-butyl)phenol	207.5	
2-(tert-butyl)phenol	205.0	243.0
4-(1-butyl)phenol	249	
4-(2-butyl)phenol[d,e]	230.0	
thymol[d,e]	204.5	
carvacrol	216.0	
2-(tert-butyl)-5-methylphenol	206.5	239.0
2,6-di-(tert-butyl)phenol[d]	172.0	
4-nonylphenol[d]	224.5	
2-chlorophenol	232.0	
2-carboxymethylphenol	190.0	234.5
2-carboxyethylphenol	187.0	239.0
2-carboxy-(2-hydroxyethyl)phenol[d]	243.5	260.0
4-cresol + n-octane (equimolar)	231.5	
Miscellaneous		
benzaldehyde	222.0	
aniline	(185.5)	
N-methylaniline	180.0	213.0
2-chloroaniline	190.5	221.5

[a] Values in parentheses from Reichardt.[11] [b] Calculated from E_T' with (4). [c] Value from Rappoport and Kaspi.[10] [d] Supercooled liquid measured at room temperature. [e] Measured at 40 °C.

solvent and made up to a volume of 5.0 cm^3 with this solvent, to produce a solution ~0.2 M (M ≡ mol dm^{-3}). This was further fourfold diluted with the solvent, and on this 0.05 M solution the NMR spectrum was run. It was confirmed by further dilution with the solvent in a number of cases, that the 0.05 M solution represents the infinite dilution value of the chemical shift. All measurements were made at the instrument temperature of 30 °C.

Results

The transition energies E_T of 2,6-diphenyl-4-(2′,4′,6′-triphenyl-1-pyridino)phenoxide (betaine dye no. 30) in approximately 50 solvents are given in Table I. This table

TABLE II: Effect of Water on the Transition Energy of Betaine Dye No. 30[c] in Various Solvents (at 23 ± 2 °C)

solvent	E_T/kJ mol^{-1} (dry solvent)	sat. concn of water[a] mol dm^{-3}	sat. concn of water[a] mol fract	E_T/kJ mol^{-1} (water sat.)
1-butanol	210.5	9.50	0.515	216.5
1-hexanol	206.5	3.36	0.313	211.5
1-octanol	203.0			208.4
2-ethyl-1-hexanol	193.5	1.20	0.162	197.5
benzyl alcohol	214.0	4.86	0.354	215.0
phenol	257	17.43	0.678	249.0
3-cresol	223	7.63[b]	0.484[b]	249.0
2,4-xylenol	213.0	7.72[b]	0.389[b]	241.5
2-(2-butyl)phenol	207.5	2.16[b]	0.258[b]	217.5
carvacrol	216.0	1.68[b]	0.211[b]	245.5
2-(tert-butyl)-5-methylphenol	206.5	0.93[b]	0.139[b]	213.0

[a] From J. A. Riddick and W. B. Bunger, "Organic Solvents", Wiley-Interscience, New York, 1970. [b] Determined in this work. [c] Reference 2a.

also gives the E_T' values of the other betaine dye studied (no. 1) for 20 solvents. In view of the good correlation found

$$E_T' = 1.00E_T + 35.0 \text{ kJ mol}^{-1} \qquad (3)$$

(within twice the combined experimental errors), it was considered unnecessary to measure E_T' for all the solvents studied. The table includes three solvents unavailable to us but studied by others, for the purpose of comparison. Many additional branched alcohols were included in the compilations of Reichardt,[2b,11] but only the lower straight-chain alcohols are found there. For the normal alcohols, the following expression represents the data for methanol to dodecanol well, within a standard deviation of ±1.2 kJ mol^{-1}:

$$E_T/\text{kJ mol}^{-1} = 76.4(n + 1)^{-1} + 194.2 \qquad (4)$$

where n is the number of carbon atoms in the chain.

The lower alcohols are, of course, miscible with water in all proportions, and so is trifluoroethanol. The E_T values of the aqueous mixtures of methanol, ethanol, and 2-propanol and E_T' for aqueous trifluoroethanol have been reported.[2b,10] The effect of water on the E_T values of the higher alcohols can be measured only to the limit of the solubility of water in them, and this is the case for all the phenols studied. Since the E_T of all these solvents is fairly high to begin with, not too different from that of water[2] (264 kJ mol^{-1}), the effect of the admixture of water is not expected to be large. As the data in Table II show this is the case, with the notable exception of carvacrol (2-methyl-5-(2-propyl)phenol).

The validity of the results obtained for the more acidic solvents in the presence of triethylamine was tested by adding varying concentrations of the base to a few solvents, as reported in Table III.

In no case was a marked effect on E_T found up to 0.1 mol dm^{-3} of base. The results confirm the observations of Rappoport and Kaspi,[10] who used 0.1 mol dm^{-3} of triethylamine in ethanol, 2-propanol, and water, without affecting the transition energy shown by the betaine dye in the pure solvent. For carvacrol, high concentrations, >0.25 mol dm^{-3}, of base cause a notable increase of E_T, as does a high concentration of water, 1.68 mol dm^{-3}. No immediate explanations of these effects are apparent.

For very acidic phenols, such as 4-chloro- or 4-fluorophenol, and for solvents even more acidic than the phenols, e.g., 2-bromobutyric acid, no $\pi \rightarrow \pi^*$ band of the betaine

TABLE III: Effect of Triethylamine on the Transition Energy E_T/kJ mol^{-1} of Betaine Dye No. 30[a] in Various Solvents

C_{Et_3N}, mol dm^{-3}	E_T 1-butanol (at 34 °C)	E_T 2-(tert-butyl)phenol (at 30 °C)	E_T carvacrol (at 25 °C)
0.000	210.0	204.5	210.0
0.031			210.0
0.063	210.0	204.5	210.0
0.125	210.0	204.5	213.0
0.250	210.0	204.5	225.0
0.500	210.0	208.0	238.0
0.75	210.0		
1.00	209.0	208.0	242.0

[a] Reference 2a.

TABLE IV: Transition Energies in kJ mol^{-1} of 4-Cyano-1-ethylpyridinium Iodide in Various Protic and Aprotic Solvents, Compared with Literature Data for Some Aprotic Solvents

solvent	Z'	E_T^e
chloroform	332.5 (316.5)[a]	231.5 (217.5)[d]
acetone	258.5 (258.5)[a]	174.5 (176.5)[d]
acetonitrile	281.5 (280.0)[a]	192.0 (192.5)[d]
1-hexanol	306.5	211.5 (206.5)[c]
1-butanol	308.5 (307.5)[b]	213.0 (210.5)[c]
ethanol	332.5 (316.5)[a]	231.5 (217.5)[c]
methanol	334.0 (331.0)[a]	233.0 (233.0)[c]
formic acid	345.5	241.5
acetic acid	331.5 (313.5)[b]	231.0
propanoic acid	330.5	230.0
1-butanoic acid	327.5	227.5
1-pentanoic acid	332.5	231.5
1-hexanoic acid	333.0	232.0
1-heptanoic acid	330.5	230.0
2-bromobutyric acid	384.0	271.5

[a] Reference 3. [b] Reference 3, calculated from Z via (5). [c] Table I. [d] Reference 2. [e] Values of E_T calculated from (6).

dyes could be observed, even in the presence of triethylamine. For a few acidic solvents, therefore, measurements were made with an indicator compound suggested by Kosower,[3] i.e., 4-cyano-1-ethylpyridinium iodide. Acetic acid is too acidic for the betaines but gave, with 4-carbomethoxy-1-ethylpyridinium iodide, a solvent-sensitive absorption peak at 361 nm. The cyano-substituted compound has a peak 20–30 nm to the red of the peak shown by the carbomethoxy compound in those solvents where it was tested.[3] The correlation

$$Z'(\text{NCC}_4\text{H}_4\text{NC}_2\text{H}_5\text{I})/\text{kJ mol}^{-1} =$$
$$0.973[Z/\text{kJ mol}^{-1}] - 8.7 \quad (5)$$

where Z' and Z are the transition energies for the cyano and the carbomethoxy compound, respectively (the basis for the standard Kosower scale), was obtained for the six solvents: pyridine, acetone, dimethyl sulfoxide, acetonitrile, ethanol, and methanol tested by Kosower.[3] Our values of Z' are shown in Table IV and compared with Kosower's data where available.

Since the correlation

$$E_T/\text{kJ mol}^{-1} = 0.774(Z'/\text{kJ mol}^{-1}) - 25.8 \qquad (6)$$

has already been found,[2b] the E_T values corresponding to the Z' values determined in this work are also given. The main drawback of the Z' (or Z) scale in the present context is its inapplicability to aromatic solvents, such as the phenols, since the relevant charge transfer absorption band of the indicator compound overlaps that of the solvent

TABLE V: Chemical Shift (δ/ppm) of Tri-n-butylphosphine Oxide (^{31}P NMR) in Various Solvents Referred to Concentrated (85 wt %) Aqueous Phosphoric Acid, Volume Magnetic Susceptibility (K_v), Derived AN and E_T/kJ mol^{-1} Values, and Independent Data on E_T

solvent	δ	$-10^6 K_v{}^a$	$\delta_{cor}{}^c$	AN(eq 7)	E_T(eq 8)	E_T(expt)
hexane	41.3	0.57	40.6	0.0^d	139.0	129.5^e
water	61.7	0.72	61.3	54.8^d	258.5	264.0^e
3-cresol	60.1	0.69	59.6	50.3	248.5	223.5^f
2-chlorophenol	60.3	0.75	59.9	51.1	250.5	232.0^f
2,4-xylenol	56.0	$(0.72)^b$	55.0	38.1	222.0	212.5^f
carvacrol	58.5	0.71	58.1	46.3	240.0	216.0^f
acetic acid	59.9	0.55	59.1	49.0 $(52.9)^d$	246.0	239.9^g
propionic acid	58.5	0.58	57.8	45.5	238.0	234^g
1-butanoic acid	58.2	0.60	57.5	44.7	236.5	232^g
1-hexanoic acid	57.8	0.62	57.2	43.9	234.5	233^g
2-bromobutyric acid	63.7	$(0.72)^b$	63.3	60.1	270.0	279^g

^{a} From "Handbook of Chemistry and Physics", 47th ed, Chemical Rubber Co., Cleveland, 1966–1967, pp E-108 to E-113. ^{b} Estimated. ^{c} $\delta_{cor} = \delta + (2\pi/3)(K_{v\,ref} - K_v)$, where $K_{v\,ref} = -0.92 \times 10^{-6}$ is the value for 85% phosphoric acid. ^{d} Values from ref 4. ^{e} Values from ref 2. ^{f} Values from Table I. ^{g} Estimated from distribution data, Y. Marcus, E. Pross, and J. Hormaldy, to be published.

itself, being too far in the ultraviolet. In order to ascertain whether any hydrolysis of the cyano group occurred while the indicator dye was in contact with the carboxylic acid solvents, a propionic acid solution of the dye was kept for 48 h at room temperature, and then the solvent was evaporated under vacuum, again at room temperature. The infrared spectrum of the residue showed only the C≡N signal, but not the C=O signal expected for hydrolysis.

Still, attack on the 4-cyano-1-ethylpyridinium iodide dye by very strongly protonating solvents could be feared. Therefore, these solvents were also measured by the nuclear magnetic resonance method, to obtain AN data.[4] Triethylphosphine oxide was unavailable to us, but tributylphosphine oxide, which was, served well, but required calibration. A two-point normalization procedure was employed following Mayer et al:[4]

$$AN = 54.8(\delta_S - \delta_{hexane})/(\delta_{water} - \delta_{hexane}) \qquad (7)$$

to obtain the acceptor number AN as a dimensionless quantity. Here, 54.8 is the AN of water, obtained with triethylphosphine oxide,[4] δ_i is the chemical shift in the solvent i (= S, water, or hexane) relative to external concentrated phosphoric acid, extrapolated to negligible concentration of the solute, and corrected for the bulk magnetic susceptibility. The values thus obtained are shown in Table V.

Of the 34 solvents studied by Mayer et al.,[4] 29 also had E_T values determined, which correlate as follows with the AN values:

$$E_T/\text{kJ mol}^{-1} = 2.182(AN) + 139.0 \qquad (8)$$

with a standard deviation of ±5 kJ mol^{-1} for the whole set. However, there are notable cases of large deviations: propylene carbonate, $\Delta = [E_T$ (calcd from (8)) − E_T (expt)]/kJ mol^{-1} = −16.5, chloroform, Δ = +26.0, and, in particular, acetic acid, Δ = +45.5. No explanation was given[4] for these deviations. The E_T values calculated from our AN data by means of (8) are also shown in Table V.

Discussion

Alkanols. For the aliphatic alcohols, sufficient experimental data have been collected in Table I and ref 2 to permit a correlation. This may be utilized to predict the E_T values, hence the solvent properties, of alcohols which have not been studied yet.

For the straight-chain alcohols, correlation (4) has already been presented. It says, in effect, that the effect on the transition energy of replacing a hydrogen atom by a

methyl group decreases the further away from the hydroxyl group this replacement is made. The following values can be given for E_T/kJ mol^{-1} for such replacements (including branching):

(a) −16.0 for methyl replacing hydrogen on the α carbon
(b) −7.0 for methyl replacing hydrogen on the β carbon
(c) −3.0 for methyl replacing hydrogen on the γ carbon
(d) −6.0 for ethyl replacing methyl anywhere
(e) −21.0 for a second methyl replacing hydrogen on the α carbon.

These generalizations may be illustrated by comparing (calculated and experimental) values of E_T/kJ mol^{-1}: (a) ethanol (217.0, 217.5), 2-propanol (203.5, 204.5), 2-butanol (197.5, 197.0), 2-pentanol (193.5, 194.5), 2-octanol (189.0, 191.0); (b) 2-methyl-1-propanol (204.5, 205.0); (c) 3-methyl-1-butanol (207.5, 208.0, the value 196.5 given in ref 2 is much too low to correspond to any systematic trend); (d) 1-propanol (211.0, 213.0), 3-pentanol (191.5, 191.0), 2-ethyl-1-hexanol (192.0, 193.5, illustrates also (b)); (e) 2-methyl-2-propanol (182.5, 183.5), 2-methyl-2-butanol (176.5, 177.5).

The procedure for determining the transition energy of any straight-chain or branched aliphatic alcohol is therefore simply: (i) seek the longest straight alkyl chain bound to the hydroxyl group; (ii) calculate E_T from (4) for this chain; (iii) apply (a–e) as corrections to obtain the final E_T values. Attempts to use, instead of the above, such well-known topological indexes of the alcohols as the Wiener number, the connectivity or branching index, or the surface area failed. The reason for this is that these indexes do not account for the inductive effect, which depends on the proximity of the branching to the functional group.

For alcohols with more than one functional group, apply the correction terms:

(f) +17.0 for hydroxyl replacing hydrogen on a methyl group
(g) ~0.0 for −O− separating parts of the carbon skeleton.

As an illustration, again, compare calculated and experimental values of E_T/kJ mol^{-1}: 1,2-ethanediol (234.5, 235.5), 1,3-propanediol (230.0, 229.5), 1,2-propanediol (222.5, 226.5), 1,2,3-propanetriol (238.5, 238.5), 3-oxa-1,5-pentanediol (226.5, 225.0), 3,6-dioxa-1,8-octanediol (222.0, 224.0), 3-oxa-1-butanol (213.5, 218.0). These prescriptions are seen to predict the experimental values within ±1.2 kJ mol^{-1} on the average.

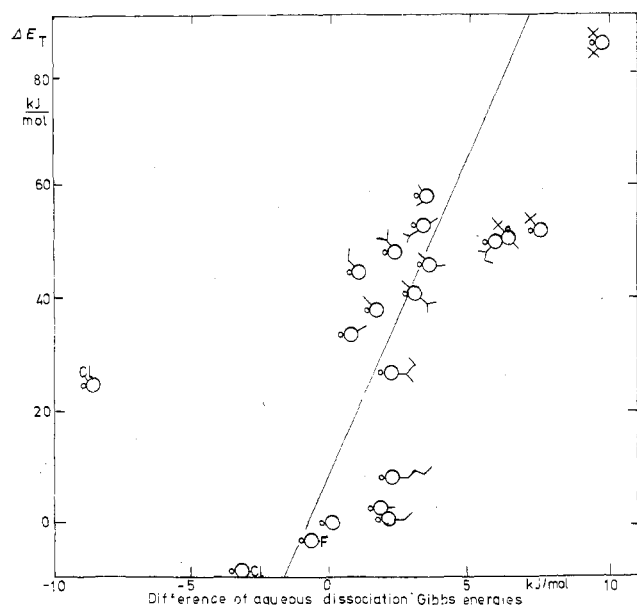The physical meaning of these effects can be understood in terms of a combination of inductive and steric effects.

Figure 1. Correlation of the transition energies (relative to phenol) of substituted phenols, ΔE_T, and their logarithms of the aqueous dissociation constants (relative to phenol), $\Delta(\Delta G°\text{diss})_{aq}$. The position and nature of the alkyl substituents are represented symbolically. The values for E_T for 4-chloro- and 4-fluorophenols were obtained from distribution data.[8]

For instance, the E_T of a tertiary alcohol is lowered by the proximity of the methyl groups to the hydroxyl, because of both the inductive properties and steric effects of these groups. Compare E_T/kJ mol^{-1} for carbinol (methanol, 233.0), methylcarbinol (ethanol, 217.5), dimethylcarbinol (2-propanol, 204.5), and trimethylcarbinol (2-methyl-2-propanol, 183.5). The more exposed the hydroxyl, and the lower the electron density on it, the better is the alkanol able to donate hydrogen bonds, and the better its solvating power toward anions. The decrease of E_T with increasing alkyl chain length, on the other hand, may be ascribed to the dilution of the hydroxyl group with the hydrocarbon chain. An equimolar mixture of ethanol with hexane should, accordingly, have approximately the same E_T as has octanol, and this is, in effect, found experimentally (see Table I).

For a few of the lower alkanols, values of Z (or Z') and AN have been published,[3,4] so that conformation to (5) and (6) and to (8) can be confirmed. The Z of 2-methyl-2-propanol corresponds to E_T/kJ mol^{-1} which is 8.5 units too high, a discrepancy which may correspond to a real effect, in that the solvating power of the strongly sterically hindered 2-methyl-2-propanol toward the iodide ion paired with the quaternary pyridinium indicator may differ from that toward the 2,6-diphenylphenoxide oxygen of the betaine indicator. Such findings lead to the cautionary remark that *the desired universality of the solvent indices may not always be achieved in practice.*

Phenols. The phenols, similarly to the alkanols, show the dilution effect, in that E_T decreases with increasing molecular weight of the alkyl phenol, provided substitution is at the same ring position. One test of this statement is the comparison of E_T of nonylphenol (mainly para substituted, with a branched nonyl group) and that of an equimolar mixture of p-cresol and n-octane, which has the same nominal molecular weight (see Table I). The dilution effect, discussed for the aliphatic alcohols, is noted here too, but this trend cannot be tested very rigorously, since there are no homologous series of *liquid* (or low melting) alkyl phenols corresponding to the normal alkanols. Hence, those alkyl phenols amenable to measurement of

their E_T are usually substituted at various ring positions with branched alkyl groups. The most clear effect is that of steric hindrance of bulky substituents in the ortho positions to the phenolic hydroxyl group. Blocking groups at both ortho positions decrease E_T drastically (compare E_T/kJ mol^{-1} for phenol (257), 2,6-dimethylphenol (199.0), and 2,6-di-*tert*-butylphenol (172.0)). With one substituent only in the ortho position and a second elsewhere, there is more scope for the inductive effect. Such effects are manifest in the substituted phenols also in the isolated molecules (gaseous state) and in aqueous solution, although these states do not represent all the aspects of the phenols as bulk liquids. Since the intrinsic acidities of substituted phenols (in the gas-state) are well correlated[13] with the acidities in aqueous solutions, and since many more pK_a values for the latter exist for comparison with the E_T values, only the latter comparison was attempted (Figure 1).

The properties of substituted phenols as liquids have been much less studied than those of the alkanols, or those of the phenols in solution in other solvents, e.g., water. However, the E_T values found here show them to be very effective hydrogen-bond donor solvents, capable of solvating small anions, such as chloride. This aspect has, indeed, been studied in the gas phase[14] and in other solvents relative to water.[15]

Carboxylic Acids. The data for the acids are not as extensive as for the alkanols and for the phenols, and no direct E_T values could be measured. These had to be estimated via (6) and (8), and these estimates are shown in Tables IV and V. It should be noted that a discrepancy exists between the two sets of estimates. According to the Z' index (Table IV), the acids are not extremely good hydrogen bond donors (electron pair acceptors): as good, say, as ethanol, but certainly not as good as phenol or as water. On the other hand, according to the AN index, the acids are better acceptor solvents than methanol, and almost as good as water. This discrepancy cannot be resolved on the basis of the present data, and may reflect some inherent differences in the properties measured by the indexes Z and AN. These acids exhibit the abnormal property of having a dielectric constant which *increases* with increasing temperatures, due to monomerization and loss of the antiparallel alignment. The basic AN indicator trialkylphosphine oxide is apparently able to effect a similar opening of the cyclic dimer, and "see" an effectively better solvent, while the iodide anion of the 4-cyano-1-ethylpyridinium Z indicator apparently cannot do so, and "sees" the dimeric, relatively poor solvent.

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Studies of the Na₂O–Na₂SO₄ System

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The behavior of Na₂O–Na₂SO₄ melts at 920 °C has been studied by four techniques: (1) chemical analysis of quenched melts, (2) manometric experiments in which the reversible uptake of O₂ by the melts was observed, (3) potentiometric studies, using oxide ion specific zirconia electrodes, and (4) voltammetry, which detects the number of oxidizable species. In oxygen atmospheres all four studies are consistent with peroxide formation in the melt, although values of the peroxide/oxide ratio vary somewhat with method. At low O₂ pressures (<0.1%), the potentiometric results are anomalous.

Introduction

Recent problems with the "hot corrosion" of superalloys, comprised principally of nickel, cobalt, chromium, and aluminum, by molten Na₂SO₄ have in the past few years spawned a large body of research work aimed at understanding the nature of the corrosion process.[1] Most of these studies have been concerned with an examination of alloys after exposure to the molten salt. There also exists, however, a much smaller body of literature concerned primarily with the study of molten sulfate chemistry.

Lux[2] seems to have been the first to recognize that molten alkali metal sulfates can be regarded in terms of the equilibrium

$$M_2SO_4 = M_2O + SO_3 \ (SO_2 + {}^1/_2O_2) \qquad (1)$$
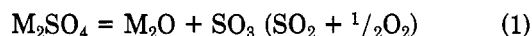
His potentiometric studies of oxides were primarily carried out in equimolar Na₂SO₄–K₂SO₄ melts at 950 °C. Flood and Forland[3] supported Lux's acid–base concepts on the basis of their work in molten sulfates. More recently, various workers[4–6] have used molten sulfates as solvents in the determination of standard potentials for various species.

A somewhat different approach to the study of oxides in molten sulfates was recently taken by Liang, Bowen, and Elliott.[7] They were interested in measuring the effect of oxides such as Cr₂O₃ on the oxide activity in molten Na₂SO₄. By inventing a reference electrode reversible to Na⁺, they were able to measure the activity of Na₂O in the melt as a function of both melt and gas composition.

In none of the above studies has the possibility of peroxide and/or superoxide formation in molten sulfates been considered. Since these species are the predominant oxides in molten nitrates[8] and at least peroxides have been

identified in molten carbonates[9] and in NaCl at 830 °C,[10] their formation in Na₂SO₄ should now also be considered. If they do exist in this salt, then additional reactions for the corrosion of metals become plausible. Manometric, chemical, potentiometric, and voltammetric studies of Na₂O–Na₂SO₄ melts similar to our earlier work on NaCl[10,11] were therefore carried out. In addition to these, we have repeated the experiment of Liang, Bowen, and Elliott[7] and examined the stability of Na₂O–Na₂SO₄ melts, i.e., reaction 1 implies that for a given gas composition, the oxide activity is fixed:

$$K_{eq} = a_{Na_2O}P_{SO_2}P_{O_2}{}^{1/2} \qquad (2)$$

since, for these dilute melts, $a_{Na_2SO_4} \approx 1$. Thus any Na₂O added to Na₂SO₄ would be expected to react with SO₂ and O₂ to maintain equilibrium. However, if SO₂ and SO₃ are absent from the gas phase, a Na₂O–Na₂SO₄ melt might be expected to persist even in the presence of O₂ (except for peroxide formation), contrary to the observation of Lux[2] that such a melt must lose Na₂O by vaporization to maintain its neutrality. Such melts were therefore carefully examined by chemical and potentiometric techniques.

Experimental Section

Most of the methodology follows our earlier work on NaCl[10] in which all melt compositions were prepared by weight. All experiments were carried out at 1190 ± 5 K. Platinum was attacked severely by basic Na₂SO₄ melts and was therefore used very little. For most experiments high-purity alumina crucibles were used since they proved reasonably inert. For example, a 1 mol % (m/o) Na₂O–Na₂SO₄ melt heated for 6–7 h (the usual time for a potentiometric experiment) had ~6% of its oxide content converted to aluminate[12] (Al₂O₃ + O²⁻ = 2AlO₂⁻), as indicated by atomic absorption measurements of quenched melts for aluminum. Since the oxide content in the po-

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