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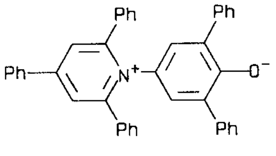
SOLVENT POLARITY SCALES. 1. DETERMINATION OF E_T AND π^* VALUES FOR PHOSPHONIUM AND AMMONIUM MELTS

W. BRIAN HARROD AND NORBERT J. PIENTA*
Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701, USA

The solvent polarity of a series of organic salts in their molten state has been determined using the solvatochromic dyes: pyridinium *N*-phenolate betaine, the basis of the E_T scale, and *N*,*N*-diethyl-4-nitroaniline, one of the primary standards for the π^* scale. Each of these dyes was dissolved in the following liquids: lithium acetate–sodium acetate–potassium acetate eutectic; ethylammonium chloride; dimethylammonium chloride; diethylammonium nitrate; ammonium trifluoracetate; tetraethylammonium acetate; tetrabutylphosphonium chloride; octyltributylphosphonium chloride; dodecyltributylphosphonium chloride; tetrabutylammonium bromide; tetrabutylphosphonium bromide; octyltributylphosphonium bromide; dodecyltributylphosphonium bromide; octyltributylphosphonium iodide; dodecyltributylphosphonium iodide; tetrahexylammonium benzoate; methyltrioctylphosphonium dimethylphosphate; and methyltrioctylammonium chloride. The ultraviolet and visible spectra were measured for each of these. In addition, data were collected as a function of temperature and in the presence of neutral and ionic additives. In general, these molten salts represent solvent polarities equivalent to moderately polar aprotic solvents such as acetone and acetonitrile. The salts with cations capable of being hydrogen bond donors gave considerably higher values, equivalent to or higher than water, the solvent with the highest value on the E_T scale. These and the eutectic mixture are thought to involve specific dye–solvent interactions which cause these anomalously high values.

The use of organic molten salts as solvents for reactions has begun to receive increasing attention. The area has been recently reviewed by Pagni[1] and Smith and Pagni,[2] and the literature before 1968 was covered by Gordon.[3] In the course of using melts as solvents for nucleophilic substitution reactions,[4–6] we surmised a need for a general way to compare the different molten salts with each other and with traditional solvents with respect to their polarity and solvating ability. A convenient way to access these properties is through the use of established solvatochromic scales, E_T and π^*. We chose the solvatochromic dye pyridinium *N*-phenolate betaine (**1**), which forms the basis of the E_T scale introduced by Dimroth and co-workers[7–9] and made popular by Riechardt and co-workers[10–15] as the primary reference. For the sake of comparison, the use of *N*,*N*-diethyl-4-nitroaniline (**2**) gave a few values for π^*, the scale developed and made popular by Kamlet, Taft, Abboud and others.[16–18]



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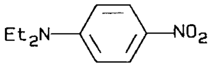

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The betaine **1** exhibits one of the largest solvatochromic effects ever observed[10] with the long-wavelength band being shifted by more than 350 nm on going from the least polar solvent (tetramethylsilane) to the most polar (water). The molecule **1** represents a so-called 'negative solvatochromism' dye whose ground state is more dipolar than its excited state. Because of its structure and this latter property, we anticipate that the solvation of this dye by molten salts should be dominated by solvent ion–solute ion interactions. The apparent significance of this will be discussed later.

The nitroaniline **2** is one of as many as 40 indicators used to establish the π^* scale, which is often used in conjunction with α and β values.[16,17] The latter two are measures of hydrogen bond donor and acceptor ability, respectively. The π^* scale is much more compressed than E_T with values generally being reported on a normalized scale between 0 and 1 (corresponding to a

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*Author for correspondence. Present address: Department of Chemistry, CB 3290, Venable Hall, University of North Carolina, Chapel Hill, NC 27599-3290, USA.

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ca 60 nm range for the dye **2**). Thus, the values of π^* for any solvent are the average of many data including statistical fits, an approach used to prevent specific solute-solvent interactions.[16,17] The shortcoming of the approach is that the measurement of an absorption maximum of a single dye (including the experimental uncertainty) may not give a very precise π^* value. The E_T dye **1** also has potential problems, especially those associated with specific solvent interactions that will be discussed later.

The salts in this study include many quaternary ammonium and phosphonium cations, generally with four alkyl groups attached to the central atom. Hence the E_T values are determined as a function of the length and structure of the alkyl chains, the central quaternary atom and the anions. A few carboxylate salts are included. Other variables include the temperature and the presence and amount of neutral or ionic additives.

RESULTS

The E_T and π^* values for the various salts considered in this study are summarized in Table 1. The entries are listed by increasing chain length of the alkyl groups attached to the quaternary center. In a number of instances three of these groups remain constant while the fourth is changed from butyl to octyl to dodecyl. A variety of anions have been considered, including halides (but excluding fluoride), carboxylates (acetates, benzoate) and others. In most instances spectral data were collected over a temperature range except for those salts that are molten at room temperature or where increasing the temperature was suspected of decomposing the melt. Only the last entry (Table 1, salt **20**) showed thermosolvatochromism, shifts in the absorption maximum as a function of temperature.

Organic salts, especially those composed of an organic cation and halide anion, are very hygroscopic. Furthermore, it has been demonstrated that the water content of solvents may have a marked effect on their E_T values.[19] In order to appreciate the relationship between the organic salts and water, a variety of data were collected. The importance of the water content was examined in a number of ways: (i) by Karl Fischer titration of various melts, (ii) by addition of water to the neat melt **13** and (iii) from aqueous solutions of the salts **13** and **15**. Figure 1 is a plot of the concentration of **13** and of **15** (done in separate experiments) in water versus the measured E_T values for the corresponding solution. The inset in Figure 1 shows the effect of molar amounts of water (0–8 M concentration of added water) on the neat salt **13**. This represents the other extreme in which relatively small amounts of water are dissolved in high concentrations of (i.e. neat) salt. Data

Table 1. Summary of E_T and π^* values for ammonium and phosphonium salts

	$R^1R^2R^3R^4Q^+X^-$ [a]								
Salt	R^1	R^2	R^3	R^4	Q	X	E_T	Temperature (°C)[b]	π^*[c]
3	—	—	—	—	Li/Na/K	CH_3CO_2	64·7	50–120	
4	H	H	H	2	N	Cl	62·3	120–50	
5	H	H	1	1	N	Cl	60·3	130	
6	H	H	2	2	N	NO_3	65·5	110	
7	H	H	H	H	N	CF_3CO_2	43·6	130	
8	2	2	2	2	N	CH_3CO_2	48·6[d]	45–90	
9	4	4	4	4	P	Cl	43·0	125–135	0·89
10	4	4	4	8	P	Cl	43·8	75–95	
11	4	4	4	12	P	Cl	42·6	90–130	
12	4	4	4	4	N	Br	43·3	105–130	0·87
13	4	4	4	4	P	Br	43·5	110–130	
14	4	4	4	8	P	Br	42·9	85–100	0·93
15	4	4	4	12	P	Br	44·5	100–130	
16	4	4	4	8	P	I	43·5	40–85	
17	4	4	4	12	P	I	42·3	50–75	
18	6	6	6	6	N	$PhCO_2$	43·9[e]	25	
19	8	8	8	1	P	Me_2PO_4	43·8	25	
20	8	8	8	1	N	Cl	44·1[f]	35–125	

[a] Groups attached to the central quaternary atom: H = hydrogen, 1 = methyl, 2 = ethyl, 4 = butyl, 6 = hexyl, 8 = octyl, 12 = dodecyl.

[b] Absorbance spectrum measured at various temperatures in the given range or at the single temperature given (see Experimental).

[c] Absorbance spectrum measured at the lowest of the listed temperatures only (see Experimental).

[d] Obtained as tetrahydrate and used without modification. For the range 100–110 °C, a value of 47·7 was obtained (see discussion in text).

[e] This value has been reported in the literature as 44·3.[10,12]

[f] Shows thermosolvatochromism: a plot of E_T versus temperature has a slope of $-0{\cdot}22$ ($r = 0{\cdot}968$, y intercept = 46·9 for a plot of six values). The listed value is that obtained at 125 °C.

on the absolute water content of some of the melts after their preparation, purification and drying were determined by Karl Fischer titrations and are summarized in Table 2. Two entries are available for each salt, one measurement obtained from the salt as it was obtained after preparation and a second in which that material was dried *in vacuo* at temperatures above 100 °C.

The betaine dye **1** is sensitive to the presence of acid. The charge-transfer nature of the solvatrochromism depends on an unprotonated phenoxide portion. The small quantity of dye required in the absorption measurement allows its protonation by surrepticious acid, especially found in halide melts.[6] Small amounts of triethylamine were added to the melt containing the dye in order to alleviate the problem. The dye's absorbance returned with addition of as little as 10 mM amine (and often less), and the observed maximum did not shift even at concentrations 5 M in amine.

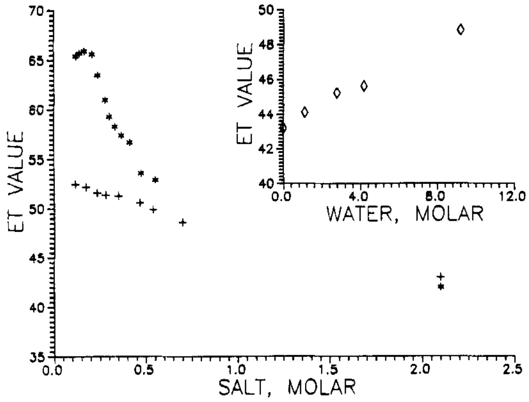

Figure 1. E_T values from aqueous solutions of **13** (*) and **15** (+). Inset: addition of water to molten Salt **13**; the highest concentration is for **8** tetrahydrate (see text)

Table 2. Karl Fischer titrations of various salts

Salt	State[a]	H_2O (wt-%)[b]	Error[c]
8[d]	W	3·50	—
9	W	1·67	0·46
9	D	0·13	0·08
13	W	1·41	0·05
13	D	0·14	0·06
15	W	1·07	0·04
15	D	0·04	—
18	W	1·17	0·07
18	D	0·46	—

[a] Pretreatment of the salt: W = used as obtained from the preparation or from subsequent storage in a desiccator, D = dried *in vacuo* at elevated temperature (See experimental).

[b] Water concentration as mol-%.

[c] Standard deviation of data in the previous column.

[d] Obtained commercially as the tetrahydrate.

The addition of long-chain hydrocarbons and alcohols has an effect on the 'order' or packing of alkyl chains in micelles, bilayers and other similar structures.[20–22] The addition of dodecane (0–0·5 M) to melts of **15** does not appear to give rise to a change in the E_T value. For example, the E_T value determined in the melts of **15** with 0·5 mM dodecane is only 0·2 units higher, well within the error limits of the measurements. Use of higher concentrations is precluded by the meager solubility of the hydrocarbon in this melt.

DISCUSSION

The solvatochromic determination of molten salt polarities provides this useful solvent property from a single, simple spectroscopic measurement. The following sections serve as an introduction; methods of determining molten salt solvent properties and a general discussion of solvatochromism precede our evaluation of the data.

Solvent properties

General discussions of organic reaction media include features such as polarity or ionizing power. In turn, these are available from dielectric constants,[23,24] dipole moments,[23,24] relative positions in elutropic series,[23,24] other microscopic measures such as donor numbers (*DN*),[25] acceptor numbers (*AN*),[25], δ,[26] and solvatochromic measures such as Z,[27] E_T,[7–15] and the trio α, β and π^*.[16,17] Traditional measures for non-polar and dipolar media (i.e. dielectric constant and dipole moments) are inappropriate for the fused salts.

Cohesive energy density and internal pressure are useful measures for interparticle interactions.[23] The former is also advantageous, since it can be used to account for mutual solubilities and miscibilities. Quantities equivalent to the cohesive energy density and the internal pressure have been assembled for fused, organic salts by Gordon,[3] and representative data are given in Table 3 together with the few Z values that have been measured for salts. A variety of traditional solvents are also included to allow comparisons, and their E_T values are reported.[10] There appears to be reasonable qualitative agreement among the various scales. However, the internal pressure scale (Table 3, column 1) requires measurement of the surface tension while the second (Table 3, column 2) uses the energy of activation for viscous flow, two quantities that are more experimentally difficult to obtain than the absorption maxima for dissolved solvatochromic dyes. In addition, these values are only available for a much more limited collection of solvents.

The use of *N*-ethyl(4-carbomethoxy)pyridinium iodide (the dye for the Z scale) has shortcomings, especially that a high concentration of contact ion pairs (CIP) of the dye is required because the measured absorption is the charge-transfer band of the CIP. Exchange of the iodide (of the *Z* scale indicator dye) with the anion of the melt greatly diminishes the absorbance peak and often removes it entirely even at high dye concentrations.[6]

The entries in Table 3 contain salts that span the entire range starting with values equivalent to moderate polarity such as methylene chloride and approaching water, the most polar entry of all of the listed standards. As the total number of carbons in the alkyl groups (on both the cation and anion) decreases, the polarity increases and the position of the salt moves down the table. For a given cation, a change in anion has a more modest effect. From the limited data (tetrapentylammonium iodide and thiocycanate; ethylammonium chloride and nitrate), it appears that the polarity of the salt increases with increasing size of the anion.

These data suggested that a more systematic study was appropriate and would enable us to probe additional variables and more subtle changes in structure. The E_T scale was chosen because of ease and convenience, and because it is possible to do a wide variety of structures (i.e. the betaine dye is soluble in most of the salts, it involves an intramolecular charge transfer unlike the *Z* dye and it does not involve estimation of molar volumes like the first two methods in Table 3).

Table 3. Solvent polarity scales[a]

Solvent	$\sigma/V^{1/3}$[b]	E_n/V[c]	Z[d]	E_T[e]	π^*[f]
Pentane	3·28	13·7	60·1	31·0	(0·0)[h]
Diethyl ether	3·60	15·5	—	34·5	0·27
$(\text{Isopentyl})_4N^+I^-$	4·06	—	—	—	—
Methylene chloride	—	—	64·7	40·7	0·82
$(\text{Pentyl})_4N^+I^-$	4·20	—	66·4	—	—
Acetone	5·57	20·7	65·7	42·2	0·71
$(\text{Pentyl})_4N^+SCN^-$	—	23·4	—	—	—
$(\text{Propyl})_4N^+$ picrate	7·37	20·4	—	—	—
Acetronitrile	7·77	—	71·3	45·6	0·75
$(\text{Ethyl})_2NH_2^+NO_3^-$	9·59	—	—	43·7[g]	—
Nitromethane	9·80	33·7	—	46·3	0·85
$(\text{Methyl})^2NH_2^+$	11·7	—	—	60·0	—
$(\text{Ethyl})NH_3^+Cl^-$	11·8	—	—	62·0[g]	—
$(\text{Ethyl})NH_3^-NO_3^-$	13·7	—	—	—	—
$Li^+/Na^+/K^+$ acetate	—	—	—	64·0[g]	—
$Tl^+CH_3CO_2^-$	13·9	—	—	—	—
$CH_3NH_3^+Cl^-$	15·4	—	—	—	—
$Tl^+HCO_2^-$	27·7	—	—	—	—
Water	27·7	236	94·6	63·1	1·09

[a] The salts were measured at various temperatures; the solvents are for 20 °C.

[b] Shown by Hildebrand and Scott[28] to be related to internal pressure.[3,23]

[c] Based on energies of activation to viscous flow[29,30] and used as a measure of cohesive energy density by Gordon.[3]

[d] Ref. 27.

[e] Refs 10 and 12.

[f] Refs 16 and 17.

[g] This work.

[h] Based on similarity to hexane and heptane for which the value is 0.[16]

Solvatochromism

The term 'solvatochromism' is used to describe the changes in position, intensity and shape of ultraviolet and visible absorption peaks that accompany variation of the solvent in which the measurement is conducted.[10,17] The changes are the result of solute–solvent interactions that alter the energy difference between the solvated ground and excited states of the dye molecules. A hypsochromic (i.e. blue) shift with increasing solvent polarity is called negative solvatochromism and corresponds to the case where the ground state of the dye is more dipolar than its corresponding excited state. Positive solvatochromism is a bathochromic (i.e. red) shift with increasing solvent polarity that occurs when the excited state is more dipolar than the ground state. The betaine **1** is a case of the former, one in which solvation by the molten salt ought to operate by ion–ion interactions.

Bayliss and McRae[31] suggest that four factors or some combination of them are important in a qualitative interpretation of solvent shifts: (i) the transition dipole moment during optical absorbance; (ii) the difference in permanent dipoles between the ground and excited states; (iii) the change in the solvent-induced ground state dipole; and (iv) the Franck–Condon principle. It has been shown that electronic polarization of the solvent molecules adjacent to a dipolar solute affects that solute's ground-state dipole, and this effect couples with the difference in permanent dipoles to give rise to the shifts.[32–36] This induced electric field has been termed a 'reaction field' by Onsager[37] and is viewed as arising from an interaction between a dipole (in this case the betaine dye **1**) and a homogeneous polarizable dielectric. Quantitative calculations of the solvent dependence of absorption maxima have been based on several models.[38] The fundamental theory has been reviewed, and critical discussions of the various models have appeared.[17]

The E_T scale has been correlated with a variety of solvent properties and with chemical reactivity in those solvents. In general, good fits in such linear free energy relationships have made the use of these values fairly general.[10,17] The E_T values have one potentially serious shortcoming that has been mentioned[10,16,17] but not quantitatively demonstrated to our knowledge. Any strong interactions with the phenoxide oxygen in dye **1** will lead to a stabilization of its ground state and a concomitant increase in the observed E_T value.[36] Hydrogen bonding is the most obvious example of such an interaction, and hydroxylic solvents have the highest E_T values. We have devised a simple way to calculate the hydrogen bonding contribution and thus 'divide' E_T

values into a polarity/polarizability component and a hydrogen-bonding component for traditional solvents.[39] (Since a number of solvent parameters or mathematical functions of them have been correlated with E_T, we perform linear regression on such pairs of values for non-hydrogen bond donors. We use the equation for that line and the solvent parameters or function of them to 'calculate' E_T. The difference between the measured and calculated values is then taken to be the hydrogen-bonding contribution.)

The π^* scale was designed to be free from specific solvent–solute interactions such as hydrogen bonding. In fact, hydrogen bond donating and accepting strengths (β and α, respectively) most often accompany the π^* values. The difficulty is that this in turn requires the use of many dyes to measure accurately a single π^* number (and even more to elicit the hydrogen-bonding values). Most of these dyes exhibit the solvatochromic effect over a narrow spectral range, and as a result small changes represent large differences in solvent properties. Nonetheless, the published π^* scale is valuable, also having been correlated in a variety of linear free energy relationships.[17] The agreement between π^* and E_T is good (especially if one excludes the solvents capable of being hydrogen bond donors[39]) and is given by

$$v_{\mathrm{ET}} = 10\cdot60 + 5\cdot12(\pi^* - 0\cdot23\delta) \qquad (2)$$

where v_{ET} is the frequency corresponding to the maximum of the E_T dye absorption (in units of $10^3\ \mathrm{cm}^{-1}$) and δ is the 'polarizability correction term' (equal to 0 for non-chlorinated aliphatic solvents, 0·5 for polychlorinated aliphatics and 1·0 for aromatic solvents).[16,17]

Molten salts as solvents

Gordon[3] described fused salts as 'ionic liquids ... composed of kinetically free ionic units.' The notion of the ion pair is not a valid one as a consequence of the strong coulombic interaction between each ion and an approximately symmetrical field of counter ions. The structure in a crystal might be considered as a reasonable model.[40]

Organic salts have an added feature to be considered, that is, the structural entity that makes them 'organic.' In the present context, these are alkyl chains surrounding the quaternary central atom in a cation or an alkyl chain in a carboxylate anion. Data from x-ray crystal structures and implications from studies of physical properties such viscosity suggest that (i) there can be penetration of the counter ion into the chain(s) of an ion (for example, an inorganic anion into the 'sphere' of alkyl groups on a phosphonium or ammonium cation); or (ii) there can be overlap in space (i.e. a tangling) of the alkyl portions of two ions.

A simple representation of the consequences of dissolving a solute in a melt are shown in Figure 2, in which part A shows no solute, part B has an ionic solute D^+—D^- and part C has a neutral molecule (shown as X—Y). The ionic solute has a minimal effect on the structure of the salt since its ions or ionic parts replace the function of that part of the molten salt. On the other hand, the neutral molecule might be expected to cause the reordering of adjacent molten salt ions by shielding them from favorable interactions with surrounding ions. From the perspective of the dissolved solute, the ionic solute (Part B) would be solvated by a microscopic environment much more like the bulk molten salt. From this simple point of view, solvatochromic dyes **1** and **2** are represented by parts B and C, respectively, in Figure 2.

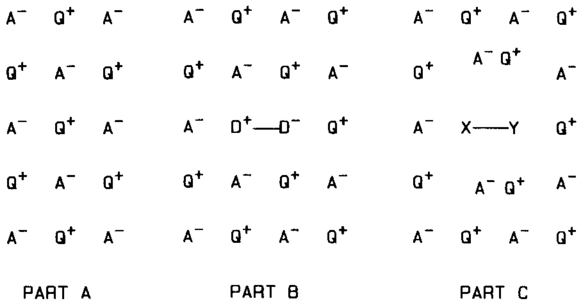

Figure 2. Representations of a simple model for molten salt with (A) no solute, (B) a zwitterionic solute, D^+—D^- and (C) a neutral solute, X—Y

One can test this model with the few data (salts **9**, **12** and **14**) for which we measured both values. By using equation (2) and the π^* values in the last column in Table 1, we calculate their E_T values as 43·3, 43·0 and 43·9, respectively. Considering the relative errors in both numbers, the small differences between these calculated values and the measured E_T values in Table 1 indicate that the differences between parts B and C in Figure 2 are not substantial, the dye **2** is not large enough to create a measureable difference or the solvent structures in parts B and C elicit the same response from the dye. Whatever the reason, we must conclude that no new specific interaction (i.e. a special solvent cavity requirement for neutral solutes) makes the π^* scale any less valid. Both E_T and π^* appear to be acceptable for highly ionic liquids.

Another important matter concerns the water content of the salts, and some appropriate data are contained in Table 2. First we consider the effects of relatively small concentrations of water in the 'neat' melts. In that context, the tetrahydrate **8** can be taken as a limiting case, since it contains the largest amount of water, and we know its water content (at least if we assume that it has not adsorbed any additional amounts). One could consider this to be a highly concentrated, aqueous electrolyte solution. Even with that as the premise, the E_T

value for that material (48·6, see Table 1) is dominated by the salt and not the water ($E_T = 63·1$, see Table 3). The remainder of the entries in Table 2 have considerably lower absolute amounts of water. They have ca 10–100 times less water if we consider them in their dried state (see column 2, Table 2) as they were used for the solvatochromic studies. It is interesting that the 'wet' state for **9**, **13**, **15** and **18** (see column 2, Table 2) appear to contain ca one water per salt molecule (although the consequences of this are unknown since their E_T values were not measured).

Koppel and Koppel[41] reported the E_T dependence of aqueous solutions containing electrolytes including **12**. Their data are related to the main portion of Figure 1 in which salts **13** and **15** are dissolved in water; **13** is tetrabutylphosphonium (TBP) bromide and **15** is dodecyltributylphosphonium (DTBP) bromide. The data for TBP starts at very high values where the salt is apparently just increasing the ionic strength of the water (i.e. the values become slightly greater than that of water itself, 63·1). At concentrations of **13** greater than ca 0·25 M, the E_T value drops precipitously as the microscope environment around **1** must become more like the salt than like water. On the other hand, the lowest concentration for **15** begins at a much lower E_T value (ca 53). The DTBP ion is a structure expected to form micelles at millimolar concentrations.[20–22,41,42] [We estimate the critical micelle concentration (CMC) for **15** to be 7–10 mM from analogous ammonium salts,[42] $R(R')_3N^+$, where $R = C_{14}, C_{16}, C_{18}$ and $R' = C_2, C_3, C_4, C_5$.] Thus, for **15** the lowest reported concentration is already an aggregate in which the dye **1** is 'dissolved.' The E_T values decrease as the size and number of the aggregates increase. The TBP ion is a poor surfactant, although it has found use in methods such as phase-transfer catalysis.[43] In analogy to mechanisms suggested for phase-transfer catalysis, we envision that the solvation of **1** by **13** occurs by association of TBP with the phenoxide portion and by van der Waals attraction of the alkyl chains with the many phenyl groups. The scarcity of literature CMC data for structures such as TBP makes it difficult to predict whether **13** will form structures like micelles at concentrations greater than about 200 mM (the concentration at which E_T drops off in Figure 1). The values at ca 2 M **13** or **15** in Figure 1 represent the E_T for the pure molten salts (i.e. the molarity of the salts themselves) and are included as a reference point. The inset in Figure 1 shows the effect of starting in the other direction, that is, by adding water to the molten salt **13**. In this case, the 'zero' water concentration is the pure molten salt and the next three points represent water added to it. The highest value corresponds to the tetrahydrate of salt **8** (see the value for **8** in Table 1).

The data of Koppel and Koppel[41] for aqueous solutions of **12** (at 25, 50 and 75 °C) agree with that illustrated in Figure 1 for **13** with two minor exceptions: (i) our value for the concentration of neat salt itself (ca 2·3 M, $E_T = 42$ at 125 °C is used as our last entry, whereas they report an E_T value for 3·2 M **12** in water (46·4 at 25 °C); and (ii) at the low concentration end, Figure 1 includes six points at concentrations below those in the previous report.[41] These entries demonstrate two important points. For the first three concentrations of **13** in Figure 1, the E_T values actually increase above that reported for water. This is consistent with the data of Koppel and Koppel[41] for aqueous solution of LiCl, NaCl, $NaClO_4$ and KBr, but perhaps for different reasons than they proposed. We suggest that at all concentrations of the inorganic salts (which show a steady increase in E_T with increasing concentration) or at low concentrations of **13** (and presumably **12**), the salt increases the ionic strength of the water and changes the associated solvent electric field. Thus, E_T rises as the 'polarity' increases. At higher concentrations of **13** (and **12**), a new trend begins to take effect: in spite of further increases in ionic strength, E_T begins to drop.

If one considers the ratio of water molecules to those of the salt at 1·0 M salt concentration (ca 50 : 1), it is difficult to imagine disruption of the bulk water structure to the extent that the E_T drops (from 60 to 45). One could envision one mechanism in which hydrogen bonding to the bromide ion competes with the dye phenoxide. That the drop in E_T is not due solely to the effect of the anion on bulk water is supported by considering the differences between **13** and **15** in Figure 1. That disparity (barring activity difference as a function of concentration between them) must be due to the structure of the cation since both are bromide salts.

In summary, organic salts (at least those composed of quaternary cations) seem to dominate the solvation of the E_T dye in water, mostly by mechanisms involving salt aggregates or preferential interactions of the salt with the dye. Nonetheless, the E_T values approach those of neat salts even when considerable water is present. We must conclude that unlike the case in traditional solvents,[19] dye **1** is not a good indicator of the water content of molten organic salts. However, we note that the forces that dominate the solvation of **1** are likely to be as great or greater for neutral organic solutes (e.g. dye **2**), and such molecules might undergo reaction in a considerably water-free region, even if water is present in the system. [Our only support for this suggestion is the lack of water addition products in substitution reactions,[4–6] a highly unremarkable observation because of the greater nucleophilicity of anionic nucleophiles (i.e. the salt anions) versus comparable concentrations of neutral water].

Effect of molten salt structure on solvatochromic values

The data in Table 1 allow a comparison of the potential effects of some of the structural variables. Salts **3**–**7** are discussed in the next section. The length of the alkyl chain, central quaternary atom and anion have been varied in **8**–**20** (a number of structural variants have been precluded because their melting points are high enough that decomposition became a concern).

With the exception of salts **8** and **20**, there is remarkably little variation in this part of the table. The acetate **8** was obtained commercially as the tetrahydrate, and although heating *in vacuo* (or just heating in the cuvette for 1–2 h) would decrease the E_T value (and presumably the water content), carrying this out for long periods of time resulted in decomposed (i.e. brown) salt. The lack of variation among **9**–**19** suggests that the microscopic environment in this series is similar. This was reassuring from the point of view of our work with halide nucleophilicities in these media.[4–6] That is, the differences among the halides are not simply due to a change in the 'bulk' properties. On the other hand, the three halides used here correspond to a considerable variation in size and polarizability of the anion. Comparison of such a series implies only small variations in average interionic distances, a result that in turn requires greater penetration of the anion into the alkyl portion of the cation on going from chloride to bromide to iodide. Again, it is possible that the E_T dye is not very sensitive to the interionic distance (see previous discussion of Figure 2). The same kinds of arguments can be made for holding an anion constant and varying the cation (or at least an R group from C_4 to C_8 to C_{12}).

We might suggest a simple model in which changes do occur at the microscopic level, but they offset each other in ways that produce no change manifested by the solvatochromic probe. Suppose that an increase in the size of the salt anion or cation does cause the distance between any pair to increase. Corresponding to this change should be an increase in the distance between the salt anion and the cation portion of **1** (D^+ in Figure 2) and/or the salt cation with the anion portion of **1** (D^-). The energy of the system should increase because all of the Coulombic attractive terms have a $1/r^2$ term. However, so do all of the Coulombic repulsive terms. In other words, all of the anion–anion and cation–cation distances may have the same distance dependence as a function of anion and cation size. There is no measurable change in 'solvation' due to offsetting changes in attractive and repulsive terms.

It is interesting to note the values for **9**, **12** and **14**, the salts in which both dyes were measured. E_T predicts a polarity order **14** < **9** < **12**, which is directly opposite that which π^* suggests. We ascribe this to coincidence, because the values appear to be within the error limits (i.e. two standard deviations for $E_T = 0{\cdot}4$ and for $\pi^* = 0{\cdot}09$).

The salts **7**–**20** compare very favorably with more traditional polar aprotic solvents (e.g. acetone, acetonitrile and nitromethane) with respect to their polarities measured here. This is consistent with the findings of studies in which these kinds of media have been used for organic reactions.[1,2,4–6,44,45] We had expected a greater effect of the long-chain alkyl groups of the cations (e.g. **19** and **20**). It appears that the coulombic interaction between the solute and the charged portion of the solvent dominates even through the 'shielding' that might be provided by the alkyl chains.

Hydrogen bonding and specific interactions

The first four entries in Table 1 are examples of salts which are not consistent with the remainder of the entries. Furthermore, their E_T values are among the highest recorded for the scale. The results from salts **4**–**6** are easy to rationalize. One would expect that they should be as or more polar than entries further down the table. Based on arguments proposed in the previous section, solvent–solute interactions should be increased in the absence of alkyl chains.

In addition, the presence of H—N$^+$ bonds in the cation predispose it to hydrogen bond to the phenoxide portion of the dye. There are strong similarities to water, a very dipolar molecule with strong hydrogen bonding capabilities. In the salt, one would not expect as strong a hydrogen bond to the dye phenoxide as in water, but this might be offset by a stronger Coulombic attraction between the dye and molten salt. Furthermore, one would expect weaker hydrogen bonds among the parts of the molten salt.

The three salts **4**–**6** would be expected to be fairly acidic because of the equilibrium in the equation

$$(RNH_3)^+ X^- \rightarrow HX + RNH_2 \qquad (3)$$

They all required triethylamine (but orders of magnitude less than was observed to produce any effect on the spectrum). In addition, an effect due to the bulk properties of triethylamine would shift the E_T dye absorption maximum in the wrong direction (i.e. to the red). Furthermore, it was possible to see the spectral changes corresponding to the deprotonation of the phenol form of **1** to the corresponding phenoxide with added amine. In very polar solvents, the phenol and phenoxide both have maxima at short wavelengths, but they are distinguishable.

The trifluoroacetate **7** is more puzzling. Its ammonium cation is free of any alkyl groups and should be a reasonable hydrogen bond donor. Perhaps hydrogen bonding to the trifluoroacetate anion is much stronger than that to the phenoxide. This is consistent with the symmetrical disposition of the two oxygens in the carboxylate compared with the phenoxide. Hydrogen bonding to the chloride and nitrate anions in **4**–**6** would be expected to be small.[46] However, the origin of this anomaly is not clear, and its resolution will no doubt require additional studies.

The eutectic **3** represents a molten salt for which a specific solute–solvent interaction other than hydrogen bonding must be in force. We have found that lithium cations are responsible.[39] Limited studies of the effects of electrolytes on E_T values in traditional solvents have been reported.[41,47,48] We have found that if one measures the changes in the E_T values of acetonitrile solutions of various concentrations of lithium, sodium or potassium acetate, one observes small changes in the solutions of the latter two that can be accounted for by the effects of ionic strength or added water. At the same concentration, Li^+ has a much larger effect. Furthermore, one reaches a plateau after the addition of only small amounts of cation and this appears to correspond to a titration of the dye **1**. Thus, **3** is a melt with a high concentration of Li^+ that is complexed not only to the negatively charged oxygen of the acetate anion of the salt but also to the phenoxide of the dye. The energetics of this complex are of sufficient magnitude to produce an effect on the E_T equivalent to strong hydrogen bonding.

Thermosolvatochromism

Thermochromism is the reversible dependence of electronic absorption on temperature.[49] Thermosolvatochromism refers to the variation of solvatochromism also based on temperature, and the theory and practical aspects of these features have been reviewed.[49–51]

The chloride salt **20** exhibited a considerable change in the peak maximum as a function of temperature. In contrast, none of the other entries in Table 1 varied by more than 0·4 E_T units for the range of temperatures reported for them. A plot of the data for **20** is shown in Figure 3. The effect is interesting in that it involves a negative slope or a regular decrease in polarity at higher temperatures. This could correspond to an untangling or straightening of the alkyl chains and/or an increase in the interionic distance. One interpretation of the lack of any difference among the different halides suggests that this distance is not an important factor. A better interpretation of the temperature effects might involve the location and role of the alkyl groups in the solvation of the dye **1**. The apparent lability of **19** (which has a cation analogous to **20**) precluded its use at other than room temperature.

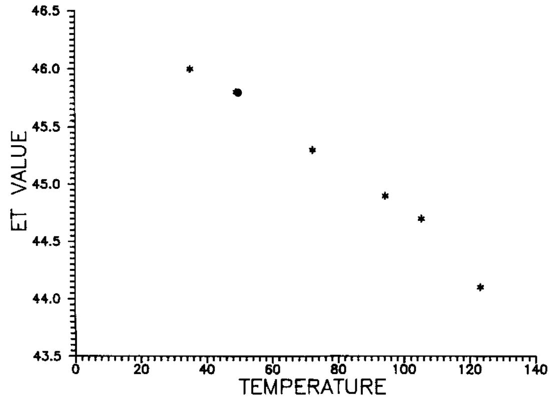

Figure 3. Temperature dependence of the E_T value for salt **20**

CONCLUSIONS

Molten organic salts of a reasonable variety of structures have been subjected to solvatochromic determination of their solvating ability or polarity. Thus, the E_T and π^* values were measured for some quaternary ammonium and phosphonium salts with different anions. There is remarkably little variation among most of them by this method with an E_T range of ca 42–44 and π^* values near 0·9. This places them in favorable comparison with polar aprotic solvents of moderate to high polarity such as acetone and acetonitrile. The use of these solvatochromic scales for molten salts must proceed with the same caveats that apply in traditional solvents. That is, the presence of hydrogen bond donors prejudices protic solvents to higher (and often much higher) values. The complexation with lithium ions has been confirmed as producing considerably higher E_T values. On the other hand, the E_T values of molten organic salts are not very sensitive to water content, in contrast to traditional solvents.

EXPERIMENTAL

Melting points were obtained using open capillary tubes in a Thomas–Hoover melting point apparatus. Melting and boiling points are uncorrected. NMR data were obtained on a Varian EM-360 (^1H) or JEOL FX-90 (^{13}C) spectrometer in the solvents listed. ^1H chemical shifts are reported in ppm relative to TMS and coupling constants (J) are reported in hertz. The ^{13}C NMR spectra are broad-band proton decoupled and are reported in ppm relative to TMS. IR data were acquired with a Perkin-Elmer Model 383 spectrometer. Analyses by gas chromatography were performed on a Hewlett-Packard Model 5730A chromatograph equipped with a flame ionization detector. The column was 10 ft × $\frac{1}{8}$ in i.d. stainless steel packed with 20% SF-96 on 60–80-mesh Chromosorb W. Prepurified nitrogen was the carrier gas (40 ml min^{-1}). Under standard conditions, the column oven temperature was linearly programmed from 60 to 220 °C at 8 °C min^{-1}.

Methylene chloride, hexane and acetonitrile were obtained from Fisher (HPLC grade) and used as supplied. 1-Chlorobutane, 1-chlorooctane, 1-chlorododecane, 1-iodooctane, 1-iodododecane, 1-bromobutane, 1-bromooctane, 1-bromododecane and tributylphosphine were commercially available or were prepared by common, standard procedures.[52] These materials were generally distilled prior to use.

Some salts were commercially available and were used without further purification: **4**, **5**, **9**, **12**, **18** and **20** from Eastman; **7** and **8** from Aldrich; and **19** from Carlisle. Salt **3** is a eutectic mixture (31% LiOAc–25% NaOAc–44% KOAc) prepared from the individual commercially available salts (Aldrich) by dissolving them in water and then removing the water *in vacuo* at elevated temperature for 24 h. The nitrate salt **6** was prepared by titrating 70% nitric acid at 0 °C with freshly distilled diethylamine (Aldrich) and removing the water from the solution at ambient temperature over ca 48 h.

Syntheses of fused salts

The Menschutkin reaction[52] of tributylphosphine (Aldrich) with each of the alkyl iodides and bromides was performed in order to obtain the corresponding phosphonium salts. Each was synthesized using procedures analogous to that described below. Reactions to obtain alkyltributylphosphonium chlorides were similar, except that they were refluxed in 50 ml of toluene for 48 h prior to workup. The salts were suction filtered and dried prior to use by heating the solid obtained *in vacuo* at elevated temperature (110 °C, 4 mmHg).

Dodecyltributylphosphonium bromide (15). Into a 100-ml round-bottomed flask fitted with a reflux condenser and magnetic stirrer, a 50 ml portion of methylene chloride, 8·4 ml (34 mmol) of tributylphosphine and 8·2 ml (36 mmol) of dodecyl bromide (Aldrich) were added. After reaction for 48 h at room temperature, the solvent was removed at reduced pressure. The last traces of solvent and excess alkyl halide were removed by washing with 50 ml of hexane. The result was a solid or often a viscous oil, which eventually solidified, in essentially quantitative yield. ^{1}H NMR ($CDCl_3$): 2·6, m, 1H; 1·6, m; 1·4, m, 4H; 0·9, t, 2H, $J = 6$ Hz.

Octyltributylphosphonium chloride (10). 1-Chlorooctane (11·6 ml, 68 mmol) and tributylphosphine (17 ml, 68 mmol) were added to 20 ml of toluene in a 100-ml round-bottomed flask which was fitted with a reflux condenser, a gas inlet tube and a drying tube filled with anhydrous sodium sulfate. The reaction mixture was refluxed for 2 days and then the solvent was removed at reduced pressure. The resulting phosphonium salt (15·5 g, 44 mmol, 65%) was obtained as a viscous oil which crystallized on standing.

Tetrabutylphosphonium bromide (13). ^{1}H NMR ($CDCl_3$): 2·5, m, 2H; 1·6, m; 1·5, m, 10H; 0·9, t, 3H, $J = 6$ Hz. M.p. 83·5–85·5 °C; lit.[53] m.p. 112 °C.

Octyltributylphosphonium bromide (14). ^{1}H NMR ($CDCl_3$): 2·5, m, 1H; 1·6, m, 4H; 1·4, m; 0·9, t, 3h, $J = 6$ Hz. ^{13}C NMR (80 °C, neat): 18·30, 17·61, 16·96, 15·44, 12·84, 10·66, 10·04, 9·00, 8·48, 6·96, 4·88, 0·42.

Octyltributylphosphonium iodide (16). ^{1}H NMR ($CDCl_3$): 2·5, m, 1H; 1·5, m; 1·4, s, 4H; 0·9, t, 3H, $J = 6$ Hz.

Dodecyltributylphosphonium iodide (17). ^{1}H NMR (CD_3CN): 2·3, m, 2H; 1·5, m; 1·3, s, 14H; 0·9, t, 3H, $J = 4$ Hz.

Karl Fischer titrations

The water content of the salts was determined by Karl Fischer titration[24] of solutions in 1,2-dichloroethane. The water content of the solvent was determined from a calibration to be less than 20 ppm. Commercial Karl Fischer reagent (Fisher) was diluted and then used for the salt assays by dissolving samples (ca 0·5 g each) in 10 ml of the solvent. Water content was determined on salts that were either pretreated or used as prepared. Thus, the titrations were carried out on salts stored in a desiccator and on samples of the same salts that had been dried *in vacuo* (130 °C, 4 mmHg, 12 h).

Solvatochromic measurements

The data were acquired by placing a standard (1 × 1 cm) quartz cell in a 4 × 4 × 4 cm aluminum block maintained at constant temperature by a 100 W (4 × 1 cm O.D.) finger heater controlled by a J-type thermocouple with a laboratory-fabricated circuit. The aluminum block was positioned such that a hole in it was aligned with the monitoring beam of a Cary Model 218 spectrophotometer. The internal temperature of the cuvette was monitored with a calibrated thermocouple thermometer. Spectra were measured (250–800 nm) on solutions made by directly dissolving one microcrystal of the E_T dye **1** (provided by Prof. Chr. Reichardt) or *N*,*N*-diethyl-4-nitroaniline **2** (Frinton Laboratories) into the sample (ca 2 ml after melting) of the fused salt contained in the quartz cell within the heated holder. The E_T values were determined as a function of temperature.[49–51] The spectra were taken after equilibration (15–30 min) at the indicated temperatures, which typically covered a range of ca 50 °C. Complete UV–visible spectra were recorded, and the maxima of the longest wavelength peak were converted to scale values.[10] The E_T value is the wavelength of the peak maximum that has been converted to the equivalent value in energy (kcal mol^{-1}). The standard deviation for the values listed in Table 1 is typically 0·2 E_T units.

The π^* values were obtained from the equation

$$\upsilon_{\max} = 27 \cdot 52 - 3 \cdot 18\pi^*$$

where $\upsilon_{\max}$ is in units of $10^3\ \mathrm{cm}^{-1}$.[16]

A few microliters of triethylamine often increased the intensity of the E_T dye's peak by scavenging acids that would protonate the phenoxide form. Control experiments showed that concentrations of about 10% triethylamine were necessary to shift the absorption maxima even a few wavenumbers. The sensitivity of the E_T values to added water was determined by control experiments that included addition of incremental amounts of water to salts, Karl Fischer titrations and spectral measurements on aqueous solutions of the salt molecules.

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