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THE POLARITY OF ALCOHOLIC ELECTROLYTE SOLUTIONS.

A SYSTEMATIC STUDY

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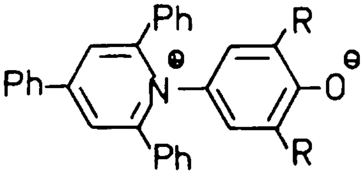
Abstract - The $E_T(30)$ polarity values of alcoholic salt solutions were determined for twenty salt/solvent combinations. In all cases equation [2] correlates accurately the medium polarity with the salt concentration. The meaning of this equation is discussed in terms of possible interactions in solution. The dye (1) is shown to be a useful probe for the cationic environment of salts in solution.

The polarity of pure solvents and solvent mixtures has long been measured with the aid of various empirical scales [1,2]. Among them, the $E_T(30)$ scale, based on the longest wavelength absorption band of the solvatochromic 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide (1), is of widespread use [1-5].



(1) R = Ph

(2) R = H

$E_T(30)$ polarity values have been determined for a large number of pure solvents, ranging from water to apolar hydrocarbons [2]. Binary solvent mixtures have also been investigated [6] and a simple empirical equation proposed, which relates the polarity of a given mixture to the molar concentration of the more polar component [7].

By contrast, the measurement of the polarity of electrolyte solutions has received little attention. Besides the studies of the polarity of micellar interfaces in surfactant solutions [4,8], a few examples of isolated systems have appeared [9-11], but little systematic effort has been made to arrive at some general treatment valid for a wide range of solutions.

In an extension of the above mentioned empirical treatment for binary solvent mixtures [7], we first suggested that electrolyte solutions could be treated in a similar way, the salt being regarded as the more polar component of a binary mixture [12]. It was shown that equation [1],

$$\ln k = \ln k_0 + A. \ln(c/c^* + 1) \qquad [1]$$

where A and c* are adjustable constants, could relate successfully the rate k of a chemical process taking place in the presence of a salt to the molar electrolyte concentration c [12].

This suggestion found further support with a study of polarity variations of various electrolyte solutions, employing system (2) as the polarity probe [13]. Our expectations that the proposed treatment should be verified for other polarity scales was later confirmed by an example where Zelinskii's polarity scale S was employed [10].

Having established that such an empirical relationship seems generally valid for electrolyte solutions, the question now arises as to the meaning of this equation and of the empirical parameters which appear in it. It is worth investigating how these parameters may reflect the nature of the salt and solvent for a particular system. It may also be asked how far one can go in treating a salt in a reasonably concentrated solution as a polar "cosolvent" in a binary liquid mixture. Clearly a closer look is needed into these assuptions, which will take into account possible interactions in solution. In order to gain some insight into these interactions, a systematic study of the polarity of alcoholic electrolyte solutions was undertaken, utilizing the $E_T(30)$ polarity scale.

RESULTS AND DISCUSSION:

Alcohols were chosen as solvents in this study for several reasons. Firstly, a variety of inorganic and organic salts could be tested, up to reasonably concentrated solutions This would also be true of water, were the phenoxide dye (1) more soluble in aqueous solutions. Unfortunately this was not the case, the dye being salted out by the addition of electrolytes. Secondly, by working with one class of solvents it would be possible to relate the variations observed, when comparing different systems, to few and essentially the same interactions.

The failure of the phenoxide (1) and other dyes to measure polarity changes of some organic electrolyte solutions with varying salt concentrations has been pointed out [10]. It was shown that aggregation of the dye in the presence of the added salt caused spectral changes which were not indicative of polarity variations. This was the case for solutions of $LiClO_4$ in acetic acid [10]. Dye aggregation probably takes place also in aqueous salt solutions of the betaine (1), leading to erroneous conclusions regarding the polarity changes of the medium with the addition of salts[14].

In alcoholic solutions, however, the addition of a salt never caused any anomalous changes in the spectra of the samples. A continuous, smooth hypsochromic shift of the longest wavelength with increasing salt concentration was always observed. This corresponded to the anticipated effect of polarity increase by the addition of an inorganic salt to alcoholic solutions (Figure 1(a)).

Equation [2] was applied with success to twenty combinations of salts and alcohols.

$$E_T(30) = E_T^O(30) + A.\ln(c/c^* + 1) \qquad [2]$$

$E_T(30)$ is the polarity value of a solution with a salt concentration c, $E_T^O(30)$ that of the pure solvent, A and c* are adjustable parameters.

Plots of $E_T(30) - E_T^O(30)$ vs. $\ln(c/c^* + 1)$, after proper adjustment of the c* value, yielded straight lines with very good correlations (Figure 1(b)).

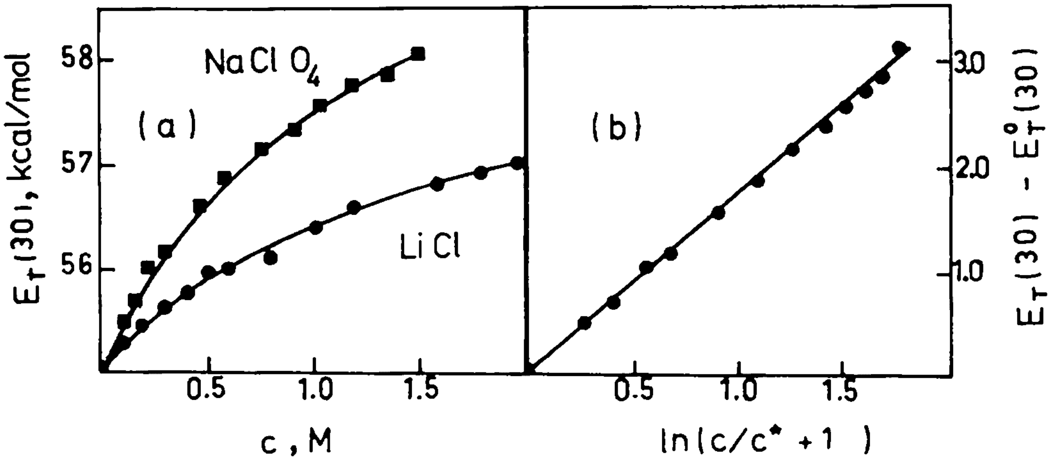


FIGURE 1. Variations of the $E_T(30)$ polarity value of salt solutions with the electrolyte concentration. (a) $NaClO_4$ and LiCl in methanol; (b) $NaClO_4$ in methanol, c* = 0.3 M, $E_T^O(30)$ = 55.5 kcal/mol.

The rate of polarity variation with the salt concentration is given by

$$d \ E_T(30) \ / \ dc \quad = \quad A/(c^* + c) \qquad [3]$$

For very dilute solutions ($c \approx 0$), the second term reduces to A/c^*. This ratio measures the effect on the medium polarity of adding a particular electrolyte to the pure solvent. For concentrated solutions, where $c \gg c^*$, equation [3] may be approximated to

$$d \ E_T(30) \ / \ dc \quad = \quad A/c \qquad [4]$$

The rate of polarity variation with the salt concentration is now dependent on c and decreases as more salt is added, thus expressing a saturation effect. Keeping the salt concentration constant, the effect on the medium polarity of adding a particular electrolyte to the concentrated solution may be gathered from the A value. Because of this saturation effect, A values alone are much less useful than the ratios A/c^* in comparing different systems, being less sensitive to the nature of the salt and of the solvent.

A direct way of comparing different salts is to calculate their $E_T^s(30)$ values. Substitution of c for the molar concentration of the pure salt, estimated from its density [15,16] and molecular weight, yields its intrinsic polarity $E_T^s(30)$.

The Table lists all the studied systems, with the corresponding values of A, c^*, A/c^* and $E_T^s(30)$. The number of data points utilized in the curve fittings and the correlation coefficients for the corresponding straight lines obtained are also given.

A first glance at the Table shows that both c^* and A/c^* values vary considerably with the nature of the salt and solvent under study. The values of A, on the contrary, exhibit a relatively narrow range of variation of ca. 1.4 kcal/mol. This shows that dilute solutions are much more sensitive than concentrated solutions to the nature of the added electrolyte.

The parameter c^* was defined previously [12,13] as a threshold concentration which separates two regions of different behaviour regarding polarity variations. The first one, for dilute systems ($c^* \gg c$), where the polarity of the system varies linearly with the concentration of added salt; the second one, for concentrated solutions ($c^* \ll c$), where the polarity of the medium varies less sharply with the logarithm of c. This threshold value is clearly rather sensitive to the nature of the salt and the employed solvent.

TABLE - Examples of alcoholic electrolyte solutions which follow equation [2] .

Salt/Solvent	Conc. range, M.	A, kcal/mol	c^*, M	A/c^*, kcal.l/mol^2	$E_T^s(30)$[a], kcal/mol	r(N)[b]
(a) NaI/MeOH	0-2.0	1.82	0.6	3.0	62.29	0.996 (14)
(b) NaI/EtOH	0-2.0	1.51	0.1	15.1	60.21	0.996 (15)
(c) NaI/1-PrOH	0-1.4	1.13	0.02	56.5	58.73	0.998 (14)
(d) NaI/1-BuOH	0-1.0	1.07	0.009	119	58.66	0.998 (14)
(e) NaI/2-PrOH	0-1.0	1.09	0.002	545	58.86	0.997 (15)
(f) NaI/2-BuOH	0-0.6	0.79	0.00009	8778	56.98	0.993 (15)
(g) LiCl/MeOH	0-2.0	1.24	0.5	3.5	61.19	0.999 (14)
(h) LiCl/EtOH	0-2.0	0.98	0.05	19.6	58.64	0.999 (14)
(i) LiCl/1-PrOH	0-1.4	1.02	0.025	40.8	58.42	0.999 (14)
(j) $NaClO_4$/EtOH	0-0.9	1.52	0.07	21.7	60.53[c]	0.998 (15)
(k) $LiClO_4$/EtOH	0-1.0	1.77	0.05	35.4	62.74	0.999 (15)
(l) $Ba(ClO_4)_2$/EtOH	0-1.0	1.07	0.0007	1529	62.08[c]	0.999 (15)
(m) $Sr(ClO_4)_2$/EtOH	0-1.0	1.03	0.0003	3433	62.49[c]	0.997 (14)
(n) $Ca(ClO_4)_2$/EtOH	0-1.0	0.72	2×10^{-6}	36×10^4	63.08	0.994 (12)
(o) LiI/MeOH	0-2.3	1.86	0.4	4.7	63.30	0.998 (14)
(p) KI/MeOH	0-0.7	1.07	0.2	5.4	60.38	0.999 (9)
(q) NaBr/MeOH	0-1.2	1.02	0.4	2.6	59.78	0.997 (10)
(r) $NaClO_4$/MeOH	0-1.5	1.68	0.3	5.6	62.61[c]	0.999 (13)
(s) LiBr/MeOH	0-0.9	1.24	0.3	4.1	61.57	0.998 (11)
(t) $LiClO_4$/MeOH	0-1.5	2.11	0.3	7.0	64.66	0.999 (13)

Footnotes: (a) - Polarity of pure salt, calculated from equation [2] and values of salt densities[15]; (b) - Correlation coefficient r for plots of $E_T(30)$ vs. ln $(c/c^* + 1)$, and number N of data points; (c) - Values of salt density from reference 16.

Effect of the Solvent - The Table presents two series where solutions of the same salts, NaI (entries (a)-(e)) and LiCl (entries (g)-(i)), have been studied in alcohols of decreasing polarities. In both series the c* value decreases with the decreasing solvent polarity. The ratio A/c* rises accordingly, being much larger, for example, in the least polar 2-butanol than in methanol for the NaI series. This probably reflects the poorer solvation of the salt, as the solvent polarity is reduced. Less solvated ionic species are comparatively more effective in increasing the polarity of the medium than highly solvated ions, the solvating molecules shielding the ionic charges in the vicinity of the solvatochromic probe. The importance of ion solvation is reinforced by the comparison of the intrinsic polarity values $E_T^s(30)$ for both series. One would expect roughly the same values for all alcoholic solutions of the same salt, but this is not the case. They decrease with the decrease of the polarity of the solvent, being in all cases smaller than the polarity value of pure water[2](63.1). However, it must not be concluded from this observation that either NaI or LiCl are less polar "solvents" than water. The decrease of the $E_T^s(30)$ values with the polarity decrease of the alcoholic solvent points to a solvation effect which shields and reduces the polarity of the naked ion. Surely a better description of the electrolyte "cosolvent" in sodium iodide solution would be the solvated salt $NaI.(ROH)_x$, and the intrinsic polarity of the more polar component will naturally reflect the nature of the solvating alcohol.

Nature of the Cation - The nature of the cation is important for the intrinsic polarity of the pure electrolyte, as can be gathered from the series of mono- and divalent perchlorates in ethanol (entries (j)-(n)) and of alkali iodides in methanol (entries (a),(o) and (p)). The A/c* ratio is much larger for divalent than for monovalent cations, increasing in the same family with the cationic charge density. This indicates that for a salt MX, where X is constant, polarity increases in the order $K < Na < Li$, and for a salt MX_2 in the order $Ba < Sr < Ca$.

Solutions of tetramethylammonium chloride in methanol and ethanol have also been examined up to a concentration of 1.5 M, but were not included in the Table because in both cases there was practically no variation of the medium polarity with the addition of the salt. This is an indication that tetraalkylammonium salts behave as less polar "cosolvents" in MeOH and EtOH. In fact, as observed before [7], the introduction of a comparatively nonpolar additive to a polar medium produces hardly any change of polarity. This observation is in line with the order of polarity of monovalent salts, the tetramethylammonium cation being larger than the least polar K^+.

An inspection of the Table shows that the A/c* and the $E_T^S(30)$ values exhibit parallel trends for almost all the given examples. The only discrepancy is found when comparing the mono- with the divalent perchlorates, entries (j)-(n). Barium perchlorate in ethanol (entry (l)) is clearly a more polar electrolyte than lithium perchlorate (entry (k)), as shown by the A/c* ratios of both systems , and by the fact that, at the same concentrations, the first salt induces larger $E_T(30)$ value shifts than the latter. Nevertheless, as judged from the $E_T^S(30)$ values of both systems, the opposite seems to be true. This observation, and the fact that the $E_T^S(30)$ value of a salt in solution depends on the solvent, show that the concept of an "intrinsic polarity" of the pure electrolyte, regarded as a hypothetical cosolvent, should be taken with some caution. This is especially true when comparing different kinds of salts, such as mono- and polyvalent electrolytes.

The order of salt polarities as a function of the cationic charge density may be analysed in two ways, as a result of salt-solvent, or of salt-dye interactions. In the first case, the added salt is regarded as changing the solvent structure , thereby changing the polarity of the medium. This "indirect" effect was invoked by Koppel and Koppel [11] to rationalize the trends observed for a few salts in water/methanol. According to the authors, structure-breaking species would increase the electrophilicity of water and cause a hypsochromic shift of the longest wavelength band of dye (1). The converse would happen with structure-making organic cations, which should thus reduce the polarity of the medium.

This particular rationalization is at variance with our observations. If it is assumed that the same order of net structure-breaking holds for the alkali cations in water and in methanol, the degree of structure-breaking in both solvents increasing with the size of the cation [17], the observed polarities of salts MX, with constant X, should augment in the order Li < Na < K. The opposite trend was observed in this work.

In the second approach, the interaction between the cation and the phenoxide dye is envisaged as the main source of the observed trends. A loose ion-pair would be formed in salt solutions of the dye, where the solvated cation would be more or less bound to the phenoxide moiety, according to the degree of cationic charge density. The measured polarity of the electrolyte solution would then reflect the ionic microenvironment around the solvatochromic probe. This second approach finds support in the studies of polarity of ethereal lithium perchlorate solutions, where the dye (1) could not be used as a polarity probe because complexation of the phenoxide end with Li^+ completely suppressed all absorptions in the visible [9]. More impressive, the analysis of spectral changes of the dye (1) in acetonitrile, when different salts were added, showed that the hypsochromic shifts of the longest wavelength band increased in the order $K^+ < Na^+ < Li^+ < Ba^{++} < Ca^{++} < Mg^{++}$.[18] exactly the same order of salt polarities observed in the present work.

The steady increase of the $E_T(30)$ value of the medium as more salt is added to an alcohol may then be interpreted as due to the gradual displacement of solvent molecules by the solvated cation in the environment of the phenoxide moiety of (1) Harder cations are more effective than softer ones in doing so, and are therefore more "polar". The large tetramethylammonium cation, with the positive charge shielded by the methyl groups, should be rather ineffective in displacing hydrogen bonded methanol molecules from the proximity of the phenoxide anion. As a consequence, alkylammonium salts are found to be less polar than methanol.

Nature of the Anion - Two series of salts with a common cation have been studied, lithium (entries (g), (s), (o) and (t)) and sodium (entries (q), (a) and (r)) salts in methanol. Both exhibit the same trend of increasing polarity with the increasing size of the anion ($Cl < Br < I < ClO_4$). Again this may be understood in terms of the cation-dye interaction discussed above. As the anion becomes larger, so does the proportion of solvent-separated ion pairs, relative to contact ion pairs in solution [19]. If it is assumed that solvated, free cations interact more strongly with the phenoxide moiety of the dye than anion-bound cations of contact-ion pairs, the observed trend is in the expected direction. This assumption is reasonable in the light of sodium-23 NMR studies of several sodium salts in non-aqueous solvents [20]. Downfield shifts were observed with increasing concentrations of salts , for those cases where contact-ion pair formation was expected. On the other hand, the shifts of methanolic solutions of the solvent-separated sodium perchlorate were concentration-independent and consistently larger, indicating a greater charge on the Na^+. Similar trends were observed in this work. We may thus conclude that the probe (1) is actually capable of distinguishing between a solvent-separated Li^+ in lithium perchlorate from a more anion-bound Li^+ in lithium chloride and, accordingly, of defining the first as more "polar" than the latter.

CONCLUSIONS:

The preceding results and discussion may be summarized as follows:

Inorganic salts behave as more polar "cosolvents" in alcoholic solutions, increasing the polarity of the medium when added to the pure solvent. By contrast, the addition of tetramethylammonium and probably other alkylammonium salts does not change the polarity of pure methanol or ethanol, these salts behaving as less polar "cosolvents" than the alcohols.

Equation [2] describes accurately the variations of polarity of the medium with the concentration of salt. Extrapolation of the $E_T(30)$ values to the molar concentration of the pure salt yields the "intrinsic" polarity value $E_T^s(30)$ of the solute. This value depends not only on the salt, but also on the solvent. Such polar "cosolvents" are therefore more aptly described as solvated ionic species.

Comparison of different salts with a given anion in the same solvent shows that, in the same family, polarity decreases with the increasing size of the cation These observations may be accomodated by a model which emphasizes the interaction between the cation and the phenoxide moiety of the solvatochromic dye (1). The dye may thus be used to "feel" the cationic environment of a salt in solution. It may be said that, by ranking pure salts according to the $E_T(30)$ polarity scale, one is primarily comparing the electron-accepting ability of the solvated cation in solution, or, to put it shorter, their electrophilicity vis-à-vis the phenoxide probe.

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EXPERIMENTAL:

UV-visible spectra were measured with a Shimadzu 210-A spectrometer, equipped with thermostatted (25.0°C ± 0.1°C), water-jacketted cell compartments.

The betaine (1) [3] was prepared from the corresponding pyridinium perchlorate , obtained in 75% yield by reaction of 2,4,6-triphenylpyrylium perchlorate [21] and the 2,6-diphenyl-4-aminophenol in dichloromethane, in the presence of triethylamine [22].

All salts employed were thoroughly dried prior to use. Concentrated stock solutions were diluted with the corresponding alcohol, both solutions containing the same concentration of the dye (ca. 10^{-4} M), and the position of the longest wavelength band determined for each resulting solution. The polarity values were calculated from $E_T(30) = 28590/\lambda$ kcal/mol, and the A and c* values adjusted with a computer program to fit the experimental data.

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