

Solvatochromic parameters of ethanolamines

Abdulkarim S. Labban and Yizhak Marcus

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

The solvatochromic parameters measuring the polarity, hydrogen bond donation (Lewis acidity) and electron pair acceptance (Lewis basicity) abilities of ethanolamine, diethanolamine and triethanolamine have been determined spectroscopically by means of suitable indicators. The degree of structure of these liquids was calculated.

The ethanolamines: monoethanolamine (MEA, 2-aminoethanol), diethanolamine (DEA, 2,2'-iminobisethanol), and triethanolamine (TEA, 2,2',2''-nitrilotrisethanol) are multifunctional substances (solvents in their liquid state) that are capable of hydrogen bonding by both donation and acceptance of hydrogen bonds. Their properties, in this respect, have not so far been determined, and it should be of interest to see how much one functional group (the one, two or three hydroxy groups) affects the behaviour of the other (the primary, secondary or tertiary amine functions). These substances are highly polar, as measured by their dipole moments, $\mu = 2.27$ D for MEA, 2.81 D for DEA, and 3.57 D for TEA, in dilute solutions in 1,4-dioxane at 25 °C ($1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}$).¹ Accordingly, their $E_T(30)$ polarity index values are also high, 52.7, 52.9 and 53.3 kcal mol⁻¹, respectively, according to Belskii *et al.*² or 51.0, 52.8 and 53.6 kcal mol⁻¹, respectively, at 25 °C (except for DEA, measured at 30 °C since its melting point is 28 °C) according to Reichardt and Schäfer.³ As liquids, these substances are highly structured⁴ (see below), as is evidenced also by their substantial viscosities: 19.3 mPa s (at 25 °C) for MEA, 352 mPa s (at 30 °C) for DEA, and 614 mPa s (at 25 °C) for TEA.¹ This feature, again, is due to the abilities of their molecules to both donate and accept hydrogen bonds, in this case from neighbouring molecules in the liquids.

Solvatochromism, *i.e.* the ability of an indicator to change its colour, depending on the solvent it is dissolved in and solvated by, has been widely used in order to describe the hydrogen-bond donation and acceptance abilities of solvents. Of the various measures (and indicators) that have been proposed for this purpose, the α and β scales of Kamlet, Taft and co-workers are viable and commonly employed,^{5,6} although not without some objections having been raised against their use. If the purpose is not to study the solvation behaviour of a given indicator molecule but rather the generalized abilities of the solvents to solvate (by hydrogen bonding) unspecified solutes, then the procedure of Kamlet, Taft and co-workers, using the average values of α and β obtained by several indicators, appears to be preferable.^{6,7} This procedure was followed in the present study. Some of the indicators that are sensitive to the α and β parameters of solvents are also sensitive to their combined polarity and polarizability, as measured by the π^* index of Kamlet, Taft, and co-workers.^{5,6} Hence, this index of the ethanolamines has also been determined.

Experimental

Materials

The solvents were used as received: MEA from BDH, AnalaR 99.0% assay, DEA from BDH, GPR reagent, >97% assay, and TEA from Fluka, 99% assay. The impurities were other

ethanolamines and water; however, in view of the considerable polarity and hydrogen-bonding abilities (see below) of the solvents, small amounts of such impurities are of little consequence in the present context. The indicators employed were of the highest purity available, and again were used without further purification. They included: *N,N*-diethyl-3-nitroaniline (**1**, Pfalz & Bauer), *N,N*-dimethyl-4-nitroaniline (**2**, Lancaster), 4-nitroaniline (**3**, Aldrich), (tetramethylethylenediamine)(acetylacetonato)copper(II) perchlorate (**4**, synthesized here⁸), 4-aminoacetophenone (**5**, Aldrich), *cis*-bis(1,10-phenanthroline)dicyanoiron(II) (**6**, synthesized here⁸) and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide (**7**, the Dimroth-Reichardt betaine 30, Aldrich).

Procedure

Dilute solutions, $0.5\text{--}2.0 \times 10^{-4} \text{ mol dm}^{-3}$, of the indicators in the solvents were prepared and their spectra were measured against solvent blanks with a Perkin-Elmer Lambda 5 UV-VIS spectrophotometer at room temperature, 25 ± 2 °C. The DEA was, at this temperature, a supercooled and highly viscous liquid, but the indicator solutions were clear and homogeneous. The wavelength, λ , of the longest-wavelength band was recorded on at least two separate solutions for each solvent-indicator combination; agreement was within 0.5 nm. The wavenumber, $\bar{\nu}/10^3 \text{ cm}^{-1} = 10^4/(\lambda/\text{nm})$, has, therefore, an uncertainty of *ca.* $\pm 0.3 \times 10^3 \text{ cm}^{-1}$. The solvatochromic parameters were calculated from the wavenumbers $\bar{\nu}$ by means of the following expressions:⁶

N,N-diethyl-3-nitroaniline **1**:

$$\pi^* = 0.452(25.52 - \bar{\nu}) \quad (1)$$

N,N-dimethyl-4-nitroaniline **2**:

$$\pi^* = 0.314(27.52 - \bar{\nu}) \quad (\text{see comment below}) \quad (2)$$

4-nitroaniline **3**:

$$\beta = 0.358(31.10 - \bar{\nu}) - 1.125\pi^* \quad (3)$$

(tetramethylethylenediamine)(acetylacetonato)copper(II) perchlorate **4**:

$$\beta = 0.358(18.76 - \bar{\nu}) \quad (4)$$

4-aminoacetophenone **5**:

$$\beta = 0.245(35.25 - \bar{\nu}) \quad (\text{see below}) \quad (5)$$

cis-bis(1,10-phenanthroline)dicyanoiron(II) **6**:

$$\alpha = 0.375(\bar{\nu} - 15.636) - 0.45\pi^* + 0.72\beta \quad (6)$$

2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide **7**:

$$E_T(30) = 2.859\bar{\nu} - \alpha = 0.0649E_T(30) - 2.03 - 0.72\pi^* \quad (7)$$

Results

The values of the observed wavenumbers, $\bar{\nu}$, and the derived solvatochromic parameters are shown in Table 1. An attempt was made to use several further solvatochromic indicators: 4-nitroanisole, 4-nitroethylbenzene, and 4-(2-nitroethenyl) anisole for π^* , 4-nitrophenol for β , and 4-cyano-1-ethylpyridinium iodide for α . Since, however, the ethanolamines have considerable absorbance in the near-UV, no spectral peaks could be observed even in short-pathlength cells when they occurred at <300 nm. These indicators were, therefore, abandoned.

In most cases, at least two values were obtained for the solvatochromic indices β and π^* , agreeing within the limits given⁶ for the use of the expressions shown above relating them to the wavenumbers, $\bar{\nu}$, so that the averages could be reported. For α , however, the two sets of values obtained for the two indicators employed diverge by more than the 2σ (σ = standard deviation) specified for the expressions,⁶ although the relative values for the three ethanolamines are retained.

Discussion

The high values of the polarity/polarizability solvatochromic parameter π^* obtained in the present study are compatible with the 'polarity' measured by $E_T(30)$ and the considerable dipole moments noted in the Introduction. Bekarek's expression:⁹

$$\pi^* = -0.573 + 14.65[(\epsilon - 1)/(2\epsilon + 1)][(n^2 - 1)/(2n^2 + 1)] \quad (8)$$

with relative permittivities, ϵ , and refractive indices, n , from ref. 1 (except ϵ for DEA, not available there, and taken as the mean of the values for MEA and TEA), permits independent estimation of the π^* values. The results are 0.92 for MEA, 0.96 for DEA and 0.97 for TEA, in substantial agreement with the solvatochromic values. The simpler expression⁵ $\pi^* = 0.03 + 0.23\mu$, devised essentially for monofunctional solvents, leads to low values for MEA and DEA, but the result for TEA, $\pi^* = 0.85$, is in substantial agreement with the other values for this solvent. Note, however, that the reported¹ dipole moments, μ , were determined in a solvent, 1,4-dioxane, that is not inert with respect to the hydrogen-bond-donating ethanolamines. Also, since the ethanolamines are highly structured (see below), the relevance of dipole moments determined in dilute solution for the behavior of the bulk liquids is questionable.

Note that the expression given above relating π^* to $\bar{\nu}$ for indicator 2 is valid for the *N,N*-diethyl derivative rather than for the *N,N*-dimethyl one actually employed. In heptane ($\pi^* = -0.08$, ref. 6) the shift in $\bar{\nu}$ between the indicators¹⁰ is

$0.59 \times 10^3 \text{ cm}^{-1}$, but in sulfolane ($\pi^* = 0.98$, ref. 6), with as high polarity as the ethanolamines, the shift is only $0.33 \times 10^3 \text{ cm}^{-1}$,¹⁰ near the uncertainty in $\bar{\nu}$, so that this shift was ignored.

The electron-pair donicity (hydrogen-bond acceptance ability) of the ethanolamines obtained with three solvatochromic indicators is consistent, although 4-nitroaniline yields somewhat divergent results, and could not be used in TEA, where the resulting $\bar{\nu}$ was much too low. The indicator 5, *i.e.*, 4-aminoacetophenone, has not been used previously to obtain β values, but its $\bar{\nu}_0$ value ($35.25 \times 10^3 \text{ cm}^{-1}$) in heptane (where $\beta = 0$) is known.¹⁰ The coefficient 0.245 was obtained in the present laboratory from studies on several donor solvents.¹¹ (Note that an error occurs in eqn. (11) of ref. 10: there should be a minus rather than a plus sign before the 5.84.)

The $E_T(30)$ values obtained here are in good agreement with those previously reported by Belskii *et al.*² and Reichardt and Schäfer.¹ The hydrogen-bond donation abilities, α , calculated from them are, however, considerably higher than those obtained by the use of the iron complex indicator, 6. The expression given above, relating $E_T(30)$ with α and taking into account also the contribution from the polarity, π^* ignores however, a possible contribution from the donicity, β , to $E_T(30)$. This can be included by using the expression:¹²

$$\alpha = 0.0692E_T(30) - 2.090 - 0.147\beta - 0.900\pi^* \quad (9)$$

This leads to the values $\alpha = 0.66$ for MEA, 0.76 for DEA, and 0.67 for TEA, which are considerably closer to the values obtained from indicator 6. Indeed, the latter values are within the combined 2σ of the relevant expressions (6) and (9).^{6,12}

It remains to discuss the relative values of the properties ascribed to the three ethanolamines. The polarity/polarizability parameter, π^* , for these liquids is higher than the values for alkanols (0.54 for ethanol⁶) or alkylamines (0.31 for *n*-butylamine), so that the multifunctionality is seen to enhance this property. A second 2-ethanol group on the nitrogen atom of 2-ethanolamine appears to have little effect, but the third group makes TEA a very polar liquid, increasing the positive nature of the nitrogen atom *vs.* the negative nature of the three oxygen atoms. This is also reflected by the reduced β value of TEA compared with MEA and DEA. On the other hand, the hydrogen-bond-donating ability, α , is maximal for DEA, whereas it is essentially equal for MEA and TEA. Each of these molecules has three hydrogen atoms available for forming such bonds, however, they are engaged with intermolecular bonding in the bulk liquid and not necessarily readily available to bonding with solutes (such as the indicators). In fact, MEA is unique in that it also has three sites for accepting hydrogen bonds (two on the oxygen and one on the nitrogen atoms), balancing exactly the donation and acceptance abilities. It is similar to water (with two sites of each kind) in this respect.¹³ TEA appears to have too many acceptance sites

Table 1 Wavenumbers of the long-wavelength bands of indicators and the derived solvatochromic parameters

indicator no.	MEA		DEA		TEA	
	$\bar{\nu}/10^3 \text{ cm}^{-1}$	parameter	$\bar{\nu}/10^3 \text{ cm}^{-1}$	parameter	$\bar{\nu}/10^3 \text{ cm}^{-1}$	parameter
1	23.75	$\pi^* = 0.84$	23.84	$\pi^* = 0.76$	23.41	$\pi^* = 0.95$
2	24.85	$\pi^* = 0.84$	24.90	$\pi^* = 0.82$		
average		$\pi^* = 0.84$		$\pi^* = 0.79$		$\pi^* = 0.95$
3	25.77	$\beta = 0.96$	26.60	$\beta = 0.69$		
4	16.43	$\beta = 0.83$	16.19	$\beta = 0.92$	17.01	$\beta = 0.63$
5	30.98	$\beta = 0.88$	31.73	$\beta = 0.82$	33.33	$\beta = 0.68$
average		$\beta = 0.89$		$\beta = 0.81$		$\beta = 0.66$
6	17.31	$\alpha = 0.47$	17.58	$\alpha = 0.61$	17.59	$\alpha = 0.48$
7	18.36	$E_T(30) = 52.5$ $\alpha = 0.77$	18.60	$E_T(30) = 53.2$ $\alpha = 0.83$	18.74	$E_T(30) = 53.6$ $\alpha = 0.76$

(seven) and is possibly more tightly internally bound than DEA (five sites), hence it is a less effective hydrogen bond donor to solutes.

The degree of structure of the solvents^{4,14} is relevant to these considerations. Their cohesion energy densities, δ^2 , the Trouton constants, $\Delta_{\text{vap}} S^\circ/R$, and the Kirkwood dipole correlation parameters, g , have already been discussed in this context.¹³ The more recently suggested measures,¹⁴ *i.e.* the heat capacity density, $[C_p^\circ(l) - C_p^\circ(g)]/V$, and the isothermal entropy of vaporization, corrected for vapour-phase interactions and relative to the isostructural alkane, $\Delta\Delta_{\text{vap}} S^\circ/R$, yield the same kind of information. The former value (in $\text{J K}^{-1} \text{cm}^{-3}$) is 1.82 for MEA at 25 °C, 1.18 for DEA at 30 °C, and 0.97 for TEA at 25 °C, whereas the limit above which a liquid is considered structured is 0.6. Indeed, MEA is more structured, according to this criterion, than most liquids, except water.

The second measure, the isothermal entropy of vaporization, is given by:

$$\Delta\Delta_{\text{vap}} S^\circ/R = [\Delta_{\text{vap}} S^\circ - \Delta_{\text{vap}} S^\circ_{\text{alkane}}]/R + (P^\circ/R)d[B - B_{\text{alkane}}]/dT \quad (10)$$

where $\Delta_{\text{vap}} S^\circ/R = \Delta_{\text{vap}} H^\circ/RT + \ln(p/P^\circ)$, $\Delta_{\text{vap}} H^\circ$ is the vaporization enthalpy, p the vapour pressure, and B the second virial coefficient at the temperature T , and P° is the standard pressure, 0.1 MPa. The alkane to which reference is made has the same skeleton as the molecule of the liquid in question, with oxygen, nitrogen *etc.* atoms substituted by carbon. For the ethanolamines this means *n*-butane for MEA, *n*-heptane for DEA and 4-propylheptane for TEA, the latter being branched, and hence a small correction has to be applied for the branching.¹⁴ Application of eqn. (10) yields for $\Delta\Delta_{\text{vap}} S^\circ/R$ of MEA 12.15 at 25 °C, of DEA 27.31 at 30 °C, and of TEA 51.52 at 25 °C. These values are extremely high, as for other

multifunctional liquids such as glycerol,¹⁴ because of the large entropic contribution of the vapour-phase interaction of these liquids at ambient conditions (4.69, 18.78 and 44.62 for MEA, DEA and TEA, respectively). But even the $[\Delta_{\text{vap}} S^\circ - \Delta_{\text{vap}} S^\circ_{\text{alkane}}]/R$ values for the liquids (7.46, 8.53 and 6.90 for MEA, DEA and TEA respectively) signify a high degree of structure, the limit above which liquids are considered structured being 2.0. It is noteworthy that the decline of the solvatochromic parameters α and β from DEA to TEA and the increase of α from MEA to DEA are reflected in the latter measures of self-interaction in the liquids.

References

- 1 J. A. Riddick, W. B. Bunger, and T. K. Sakano, *Organic Solvents*, Wiley-Interscience, New York, 4th edn., 1986.
- 2 V. E. Belskii, L. A. Kudryavtseva, L. S. Novikova, N. A. Shishkina, K. A. Derstuganova and B. E. Ivanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, **9**, 2089.
- 3 Ch. Reichardt and G. Schäfer, *Liebigs Ann.*, 1995, 1579.
- 4 Y. Marcus, *J. Solution Chem.*, 1992, **21**, 1217.
- 5 M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.
- 6 Y. Marcus, *Chem. Soc. Rev.*, 1993, **21**, 409.
- 7 Y. Marcus, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1015; 1751.
- 8 A. A. Schilt, *Inorg. Synth.*, 1970, **12**, 247, Y. Fukuda and K. Sone, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 465.
- 9 V. Bekarek, *J. Phys. Chem.*, 1981, **85**, 722.
- 10 P. Nicolet and Ch. Laurence, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1071.
- 11 Y. Marcus, unpublished results, 1996.
- 12 Y. Marcus, *J. Solution Chem.*, 1991, **20**, 929; *cf.* erratum, correcting eqn. (7) in that paper.
- 13 Y. Marcus, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 427.
- 14 Y. Marcus, *J. Solution Chem.*, 1996, **25**, 455.

Paper 6/05521D; Received 7th August, 1996