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Kamlet−Taft Solvatochromic Parameters of Eight Alkanolamines[†]

Anthony F. Lagalante,* Melanie Spadi, and Thomas J. Bruno

National Institute of Standards and Technology, Physical and Chemical Properties Division 838.01,
325 Broadway, Boulder, Colorado 80303

The frequency maxima of four solvatochromic probes were measured (25, 50, and 75 °C) in eight liquid alkanolamine solvents. Additionally, the indices of refraction of the alkanolamine solvents were measured. The frequency maxima were used to calculate solvatochromic interaction parameters. The values of the solvatochromic parameters did not vary greatly from one alkanolamine to another; however, the values of the solvatochromic parameters were high, indicating strong interaction abilities in these solvents.

Introduction

Alkanolamines represent a class of compounds that have been used in a wide variety of industrially important processes that include natural gas stripping, adhesives, paint stripping, acid neutralizers, surfactants, derivatives in drug formulations, and electrocoating.[1] Alkanolamines are commonly used by the natural gas industry to remove hydrogen sulfide, carbon dioxide, and other acid gases to “sweeten” natural gas. Generic alkanolamines, such as monoethanolamine and diethanolamine, are used in low aqueous concentrations (15% and 30 mass %, respectively) due to their corrosive nature. Functionalized alkanolamines, such as methyldiethanolamine, are less corrosive and can be used in concentrations up to 50 mass %, resulting in increased gas-treating capacity. The selectivity and acid gas removal capacity of functionalized alkanolamines can lead to reduced capital costs (smaller pipes, pumps, and vessels) in comparison to those of generic alkanolamines. Prediction of thermodynamic and kinetic data associated with removal of acid gas by alkanolamine solutions is paramount to evaluating the stripping ability of a functionalized alkanolamine. Likewise, other applications for novel alkanolamines require thermophysical data for assessment of potential replacement advantages.

Solvatochromic interaction parameters have been used to model thermodynamic and kinetic data. One of the most comprehensive solvent scales to date is the Kamlet−Taft solvent scale. The parameters of the Kamlet−Taft solvent scale quantify the solvent’s hydrogen bond donor ability α, the hydrogen bond acceptor ability β, and the dipolarity/polarizability π^*.[2−4] The Kamlet−Taft values numerically quantify solvent−solute interactions that are representative in all types of solution equilibria by measuring a specific interaction that is local to the solvation shell about a dissolved solvatochromic solute. The parameters have been used extensively in linear solvation energy relationships (LSERs) to predict solution equilibria.[5−9] Solvatochromic parameter methods have recently been shown to be statistically better than UNIFAC structural group methods for predicting infinite dilution activity coefficients of alkanes in various solvents.[10] We envision that the Kamlet−Taft parameters for the alkanolamines reported herein can be used to develop LSERs to provide insight into the important molecular interactions in alkanolamine applications, and to be used as a guide for future alkanolamine functionalization.

Experimental Section

Chemicals. Probe molecules, 4-nitroanisole (**1**), 4-nitrophenol (**2**), 4-nitroaniline (**3**), 2,6-diphenyl-4-[2,4,6-triphenylpyridinio]phenolate inner salt (Reichardt’s Dye, **4**), and *N*,*N*-dimethyl-4-nitroaniline (**5**), were obtained from commercial suppliers and were used as received. The alkanolamine solvents, monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monomethylethanolamine (MMEA), methyldiethanolamine (MDEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), and triisopropanolamine (TIPA), were obtained from a commercial supplier and were used as received. The stated purities of all alkanolamines were >99%.

Measurement of Solution Spectra. The spectra of the solvatochromic probes were measured in matched quartz cuvettes on a dual-beam, high-resolution, ultraviolet−visible spectrophotometer. The cuvette holder was a black-anodized aluminum block that was thermostated (±0.1 °C) with a circulating water bath. Each solvatochromic probe was dissolved directly in the liquid alkanolamine in a quartz cuvette (1 cm path length), and the concentration was adjusted to 0.4 and 0.8 absorbance units at the peak maximum. A reference cuvette containing the pure alkanolamine was used in all measurements. Both the reference and the sample cuvette holders were initially thermostated at 75 °C to facilitate dissolving the solvatochromic probes. After the spectra of all four solvatochromic probes were measured at 75 °C, the cuvette holder was thermostated at 50 °C and all probe spectra were measured, and finally all probe spectra were measured at 25 °C. The spectra of the solvatochromic probes in the alkanolamines were measured at a resolution of 0.05 nm per data point. Four spectra of each probe were measured, and the average peak maximum was calculated. The cuvettes were cleaned and oven-dried between the measurements of each alkanolamine solvent.

Measurement of the Index of Refraction. The index of refraction at the sodium D-line was measured using a commercial Abbe-prism refractometer thermostated (±0.1 °C) with a circulating water bath.

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* To whom correspondence should be addressed. Fax: 303-497-5224. E-mail: lagalant@boulder.nist.gov.

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Table 1. Frequency Maxima of Solvatochromic Probe Molecules ±2sd and Refractive Indices for the Alkanolamines

	($\times 10^3$ cm^{-1})				
t (°C)	$\nu(\mathbf{1})$	$\nu(\mathbf{3})$	$\nu(\mathbf{4})$	$\nu(\mathbf{5})$	n_D
			MEA		
25	31.473 ± 0.018	25.783 ± 0.007	18.136 ± 0.010	24.662 ± 0.007	1.4837
50	31.562 ± 0.016	25.881 ± 0.009	17.892 ± 0.009	24.787 ± 0.007	1.4772
75	31.708 ± 0.020	26.054 ± 0.012	17.634 ± 0.006	24.919 ± 0.011	1.4708
			DEA		
25	31.849 ± 0.020	26.148 ± 0.019	18.576 ± 0.009	24.932 ± 0.006	1.4763
50	31.964 ± 0.014	26.260 ± 0.008	18.501 ± 0.008	24.968 ± 0.017	1.4688
75	31.982 ± 0.006	26.378 ± 0.013	18.277 ± 0.007	25.141 ± 0.018	1.4615
			TEA		
25	31.953 ± 0.010	26.234 ± 0.004	18.779 ± 0.014	25.003 ± 0.010	1.4837
50	32.019 ± 0.012	26.374 ± 0.015	18.483 ± 0.007	25.025 ± 0.011	1.4772
75	32.100 ± 0.006	26.424 ± 0.010	18.124 ± 0.012	25.087 ± 0.014	1.4708
			MMEA		
25	31.965 ± 0.004	26.121 ± 0.014	18.471 ± 0.011	24.945 ± 0.004	1.4366
50	32.143 ± 0.010	26.338 ± 0.07	17.842 ± 0.020	25.221 ± 0.015	1.4272
75	32.236 ± 0.010	26.747 ± 0.014	17.213 ± 0.014	25.520 ± 0.005	1.4178
			MDEA		
25	31.902 ± 0.018	26.369 ± 0.014	18.164 ± 0.013	24.912 ± 0.009	1.4674
50	31.934 ± 0.014	26.444 ± 0.010	17.835 ± 0.008	25.032 ± 0.003	1.4585
75	32.027 ± 0.018	26.660 ± 0.006	17.483 ± 0.008	25.235 ± 0.057	1.4494
			MIPA		
25	31.781 ± 0.016	25.903 ± 0.004	18.285 ± 0.012	25.163 ± 0.006	1.4459
50	31.877 ± 0.012	26.087 ± 0.010	17.887 ± 0.008	25.268 ± 0.004	1.4357
75	31.933 ± 0.018	26.445 ± 0.018	17.297 ± 0.020	25.364 ± 0.006	1.4259
			DIPA		
25	32.289 ± 0.010	26.617 ± 0.009	17.698 ± 0.006	25.506 ± 0.004	1.4612
50	32.370 ± 0.006	26.767 ± 0.003	17.215 ± 0.008	25.545 ± 0.003	1.4521
75	32.432 ± 0.006	26.903 ± 0.003	16.886 ± 0.005	25.587 ± 0.008	1.4427
			TIPA		
25	32.422 ± 0.013	26.626 ± 0.013	17.321 ± 0.004	25.283 ± 0.006	1.4646
50	32.468 ± 0.008	26.840 ± 0.009	16.971 ± 0.003	25.546 ± 0.007	1.4459
75	32.599 ± 0.017	27.028 ± 0.007	16.551 ± 0.012	25.589 ± 0.007	1.4477

Results

The temperature-dependent frequency maxima of the solvatochromic probes in the alkanolamines and the indices of refraction of the alkanolamines are presented in Table 1. The reported standard deviation (sd) in the table is multiplied by a coverage factor of 2.0.[11] The standard uncertainty (2sd) in the reported index of refraction (n_D) measurement is ±0.0002. Values of the index of refraction are used to calculate "excess index of refraction" parameters, which are commonly used in LSER models as a correction to the π^* term.[12]

Although the data for DEA (25 °C), DIPA (25 °C), and TIPA (25, 50 °C) are below the melting points of these alkanolamines, the liquid phase persisted for a long duration (1 day) before crystallizing. These alkanolamine measurements are therefore conducted in the supercooled, metastable-liquid portion of the phase diagram.

Solvatochromic Parameter Calculations. In the calculation of the solvatochromic interaction parameters, we have chosen to replace select solvatochromic equations of Kamlet and Taft[3,4,13] with the temperature-dependent solvatochromic equations of Laurence and Nicolet.[14,15] The temperature-dependent solvatochromic equations allow for determination of interaction parameters for solvents which are solids at ambient conditions. In eqs 1−9, the electronic transition frequency (ν) of any solvatochromic probe is expressed in units of 10^3 cm^{-1}. The π^* value of a solvent is calculated using the transition frequency maximum of a non-hydrogen-bonding solvatochromic probe in the solvent (ν_{solvent}), relative to the frequencies of the probe in cyclohexane ($\nu_{\text{cyclohexane}}$) and dimethyl sulfoxide (ν_{DMSO}),

$$\pi^* = \frac{\nu_{\text{solvent}} - \nu_{\text{cyclohexane}}}{\nu_{\text{DMSO}} - \nu_{\text{cyclohexane}}} \tag{1}$$

The respective expressions to calculate π^* values using the non-hydrogen-bonding probes (**1** and **5**) are then

$$\pi^*(\mathbf{1}) = \frac{\nu(\mathbf{1}) - 34.12}{-2.40} \tag{2}$$

$$\pi^*(\mathbf{5}) = \frac{\nu(\mathbf{5}) - 28.18}{-3.52} \tag{3}$$

In reevaluating numerous β scales, Laurence selected specific non-hydrogen-bond acceptor solvents for the reference line to minimize errors in the solvatochromic values for slightly polar bases and highly polar bases.[14] The recommended solvatochromic probe pairs for calculating β values are **1** and **2** (OH donor) and **3** and **5** (NH donor). The two pertinent equations for the reference lines are

$$\nu(\mathbf{1}) = 1.0434\nu(\mathbf{2}) - 0.57 \tag{4}$$

$$\nu(\mathbf{3}) = 0.9841\nu(\mathbf{5}) + 3.49 \tag{5}$$

The β value of a solvent is proportional to its displacement from the reference line for a solvatochromic probe pair. The magnitude of the displacement from the reference line is the difference between the observed electronic transition and reference line value from eq 4 or 5. For example, using eq 5, the deviation from the reference line $\Delta\Delta\nu(\mathbf{3}-\mathbf{5})$ is calculated from

$$-\Delta\Delta\nu(\mathbf{3}-\mathbf{5}) = \nu(\mathbf{3})^{\text{calc}} - \nu(\mathbf{3})^{\text{obs}} = 0.9841\nu(\mathbf{5}) + 3.49 - \nu(\mathbf{3}) \quad (6)$$

To organize $\Delta\Delta\nu(\mathbf{3}-\mathbf{5})$ values into a usable solvatochromic scale, the deviation from the reference line for a strong base (hexamethylphosphoramide) is assigned a β value of 1.00. Thus, it is the ratio of the deviation in a given solvent to the deviation of hexamethylphosphoramide (HMPA) that is used to calculate a β value.

$$\beta = \frac{-\Delta\Delta\nu(\mathbf{3}-\mathbf{5})_{\text{solvent}}}{-\Delta\Delta\nu(\mathbf{3}-\mathbf{5})_{\text{HMPA}}} = \frac{\Delta\Delta\nu(\mathbf{3}-\mathbf{5})_{\text{solvent}}}{2.759} \quad (7)$$

Although Laurence suggested the use of the **1**−**2** homologue for the measurement of β values, we found that in the alkanolamine solvents studied, $\nu(\mathbf{2})$ occurs at lower frequencies than those in all the other solvents reported. For example, in monoethanolamine $\nu(\mathbf{2}) = 24210\ \text{cm}^{-1}$ and $\beta = 4.17$ ($-\Delta\Delta\nu(\mathbf{1}-\mathbf{2})_{\text{HMPA}} = 2000\ \text{cm}^{-1}$). This value for β is largely off scale in comparison with those of other strong hydrogen bond acceptor solvents; thus, the use of probes **1** and **2** is not recommended for measurement of the β values for the alkanolamines. Probes **3** and **5** gave β values in accord with the values typically observed in alcohol solvents, and therefore these probes were used in eq 7 to calculate β values.

A reference line and equation for α values were established by Kamlet and Taft using probes **1** and **4**.[2] The pertinent equation is

$$-\Delta\Delta\nu(\mathbf{4}-\mathbf{1}) = \nu(\mathbf{4})^{\text{calc}} - \nu(\mathbf{4})^{\text{obs}} = 1.873\nu(\mathbf{1}) - 74.58 + \nu(\mathbf{4}) \quad (8)$$

The scale was normalized to methanol (α = 1.00) using

$$\alpha = \frac{-\Delta\Delta\nu(\mathbf{4}-\mathbf{1})_{\text{solvent}}}{-\Delta\Delta\nu(\mathbf{4}-\mathbf{1})_{\text{methanol}}} = \frac{-\Delta\Delta\nu(\mathbf{4}-\mathbf{1})_{\text{solvent}}}{6.24} \quad (9)$$

Results for the calculated solvatochromic parameters are presented in Table 2. The standard uncertainty of the reported values is ±0.05 units.

Discussion

The results of Table 1 show that, for the solvatochromic probes **1**, **3**, and **5**, a shift to higher frequencies (hypsochromic) occurs with increasing temperature, while for **4** a shift to lower frequencies (bathochromic) occurs with increasing temperature. It is difficult to predict the magnitudes of the solvatochromic shifts of the hydrogen bond donor and hydrogen bond acceptor probes with temperature. This is due to the competing effects of both the hydrogen bond formation equilibrium between the probe and the solvent and the autoassociation equilibrium. Another complicating factor in the thermosolvatochromic approach is that the relative intensities of vibrational bands that are superimposed under the absorption band can skew the measured absorption band maximum.[15]

In the design of their solvatochromic scales, Kamlet and Taft suggested that a number of different values be determined for each individual solvatochromic parameter using different solvatochromic probes and that an average value of the solvatochromic parameter be reported. In our study, we have determined two values of π^*, which in almost all cases are indistinguishable within the standard uncertainty of the measurement. The magnitudes of all three solvatochromic parameters are large on the Kamlet−Taft scale, indicating strong interactions occur in solution-based processes in these solvents. The measured π^* values are high, yet the alkanolamines do not possess double bonds or permanent ring structures. This may be due to the ability of the alkanolamines to exist in both the open chain and gauche configurations in solution.[16] The magnitudes of the β values are on the order of those of alkylamines, and the α values are on the order of those of other normal alcohols, as might be expected of a compound that possesses both such functionalities.

Table 2. Solvatochromic Parameters of the Alkanolamines

parameter	25 °C	50 °C	75 °C
MEA			
$\pi^*(\mathbf{1})$	1.10	1.07	1.00
$\pi^*(\mathbf{5})$	1.00	0.96	0.93
β	0.72	0.73	0.71
α	0.40	0.39	0.39
DEA			
$\pi^*(\mathbf{1})$	0.95	0.90	0.89
$\pi^*(\mathbf{5})$	0.92	0.91	0.86
β	0.68	0.65	0.67
α	0.59	0.61	0.58
TEA			
$\pi^*(\mathbf{1})$	0.90	0.88	0.84
$\pi^*(\mathbf{5})$	0.90	0.90	0.88
β	0.67	0.63	0.64
α	0.64	0.62	0.59
MMEA			
$\pi^*(\mathbf{1})$	0.90	0.82	0.79
$\pi^*(\mathbf{5})$	0.92	0.84	0.76
β	0.69	0.71	0.67
α	0.60	0.56	0.48
MDEA			
$\pi^*(\mathbf{1})$	0.92	0.91	0.87
$\pi^*(\mathbf{5})$	0.93	0.89	0.84
β	0.59	0.61	0.60
α	0.53	0.49	0.46
MIPA			
$\pi^*(\mathbf{1})$	0.97	0.93	0.91
$\pi^*(\mathbf{5})$	0.86	0.83	0.80
β	0.85	0.82	0.73
α	0.52	0.48	0.40
DIPA			
$\pi^*(\mathbf{1})$	0.76	0.73	0.70
$\pi^*(\mathbf{5})$	0.76	0.75	0.74
β	0.72	0.67	0.64
α	0.58	0.52	0.49
TIPA			
$\pi^*(\mathbf{1})$	0.71	0.69	0.63
$\pi^*(\mathbf{5})$	0.82	0.75	0.74
β	0.63	0.65	0.60
α	0.56	0.51	0.49

In general, it can be stated that the Kamlet−Taft solvatochromic parameters do not vary greatly from one alkanolamine to another. However, some small differences can be observed within alkanolamine series where only a single functionality is systematically varied. Upon examination of the two series MEA, DEA, TEA and MIPA, DIPA, TIPA, the π^* and β values decrease slightly with an increase in the number of alkanol groups about the amine, while the α values increase slightly with the number of alcohol groups. This trend can be rationalized by the intramolecular hydrogen bonding in the alkanolamines. In aqueous solutions of alkanolamines, OH···N intramolecular hydrogen bonding is known to predominate.[16] For the monoalkanolamines (MEA, MIPA), if a percentage of the solvent molecules are engaged in intramolecular hydrogen bonds, both the hydrogen bond donor and hydrogen bond acceptor sites of the alkanolamine will be unable to engage in hydrogen bond formation with the solvatochromic probes. Functionalization with additional alcohol groups will provide an additional site for hydrogen bond donors (even if the molecule is engaged in an intramolecular hydrogen bond), and the α value will increase as observed. It is interesting to note that the α values for the di- and trifunctionalized alkanolamines are almost identical. This is to be expected because these additional alcohol groups cannot participate in further intramolecular hydrogen bonds. Along this line of reasoning, the β values decrease because the functionalization with additional alcohol groups will statistically increase the probability of intramolecular hydrogen bonding, rendering the amine group incapable of engaging in a hydrogen bond acceptor role.

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