ISSN 1407-7353 | MATERIAL SCIENCE AND APPLIED CHEMISTRY / MATERIĀLZINĀTNE UN LIETIŠĶĀ ĶĪMIJA | 2008-7353

DETERMINATION OF SOLVENTS CHARACTERISTICS BY COMPARISON THE 4-AZA-2-(4'-DIMETHYLAMINOBENZYLIDENE)-1,3–INDANEDIONE AND 2-(4'-DIMETHYLAMINOBENZYLIDENE)-1,3–INDANEDIONE SOLVATOCHROMY

SOLVENTU RAKSTUROJUMU NOTEIKŠANA SALĪDZINOT 4-AZA-2-(4'-N,N-DIMETILAMINOBENZILIDEN)-1,3-INDANDIONU UN 2-(4'-N,N-DIMETILAMINOBENZILIDEN)-1,3-INDANDIONE SOLVATOHROMIJU

Valdis Kampars, professor, Dr.hab.chem.
RTU, Faculty of Material Science and Applied Chemistry
Address: Azenes street 14/24, Riga, LV-1048, Latvia
Phone: +371 7089224, Fax: +371 7615765
E-mail: kampars@ktf.rtu.lv

Pauls Janis Pastors, researcher, Dr.chem.
RTU, Faculty of Material Science and Applied Chemistry
Address: Azenes street 14/24, Riga, LV-1048, Latvia
Phone: +371 7089394,
E-mail: pauls@ktf.rtu.lv

Key words: solvatochromy comparison, solvent H-bond donor properties

Introduction

The changes in the position or intensity of absorption bands reflect both specific and non-specific interactions between solute and surrounding solvent molecules and are often used as an easy measurable characteristic of pure or mixed solvents [1,2]. One of the most successful quantitative treatments of solvent effects on the UV-VIS absorption maximum is the multiparametric equation introduced by Kamlet and Taft [3]. The solvation interaction at a molecular level is described empirically by solvatochromic solvent parameters π^*, α, and β, where π^* represented stabilisation by virtue of non-specific dielectric interactions, including a blend of polarity and polarisibility of the solvent, α represented the stabilisation by H-bond between solute and solvent as a hydrogen bond donor (HBD) and β represented the stabilisation by H-bond between solute and solvent as a hydrogen bond acceptor (HBA). Full Kamlet – Taft equation include some other parameters such as δ - polarizability correction term for polychlorinated alyphatic and all aromatic solvents, δ_h – Hildebrand solubility parameter (the cavity term) and ξ - a coordinate covalence measure:

$$h\upsilon = h\upsilon_o + s(\pi^* + d\delta) + a\alpha + b\beta + h\delta_h + e\xi \quad (1)$$

The s, d, a, b, h and e are solute depending coefficients that represented the susceptibility towards above mentioned stabilisations respectively. To obtain information about definite stabilization effect Kamlet and Taft use solvatochromic comparison method and appropriate indicators, because structurally different probes give the possibility to detect different aspects of total solvatochromy and allow reduce the equation 1 to a simple one- or two-parameter form. The purpose of this work is to obtain a new information about HBD properties of solvents by comparison the solvatochromy of 2-(4'-N,N-dimethylaminobenzylidene)-1,3-

indandione (DMABI) and 4-aza-2-(4'-N,N-dimethylaminobenzylidene)-1,3-indandione (4NDMABI).

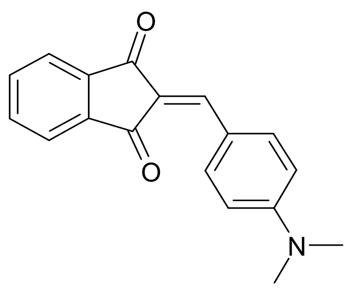
Experimental

IS spectra were recorded on a FT-IR NICOLET 5700. ^{1}H NMR spectra were obtained with Varian Mercury 200 MHz spectrometer using hexamethyldisiloxsane as an internal standard (δ=0,05), the chemical shifts were reported in δ values in $CDCl_3$. Absorption spectra were recorded on a Perkin-Elmer UV-VIS Lambda 35 with 0,1 nm accuracy.
Fluka solvents ≥99% are used without cleaning or drying. The maximum wavelength of the lowest energy band was determined by peak detection algorithm.

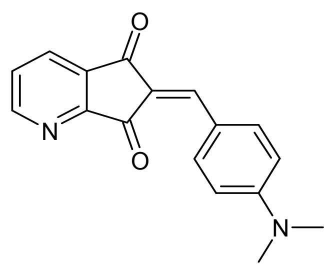
4-Aza-2-(4'-N,N-dimethylaminobenzylidene)-1,3-indandione (4NDMABI). 2,5 g (10 mM) sodium salt of indan-1,3-dione-2-carboxylic acid ethyl ester was dissolved in mixture of 7,5 ml anhydrous acetic acid and 1,25 ml of sulphuric acid. Mixture was warmed with stirring up to 50^0 C. Then by portions was added 1,49 g (10 mM) of p-N,N-dimethylaminobenzaldehyde. At the some temperature heat ten minutes. Reaction mixture was too cooled and then filtered, dried and recrystallized from acetic acid. Yield of product m=1,3 g (47%) m.p. 226^0C (decompose). ^{1}H NMR ($CDCl_3$): 3,16 (6H, s, CH_3); 6,677 (2H, m, aroma. –CH); 8,98 (1H,m, pyridines –CH); 8,19 (1H, s, C=CH); 7,8(1H, m, pyridines –CH); 7,56 (1H,m, pyridines –CH); 8,54(2H, d, aroma. –CH).
DMABI were synthesized following a literature procedures [4].

Results and discussion

DMABI is well known second-order nonlinear optical chromophore with a relatively high molecular zero frequency hyperpolarizability $\boldsymbol{\beta_0}$ = 38 x 10^{-30} esu [5]. Both DMABI, and 4NDMABI have an intensive long wavelength absorption (Fig.1). In contradistinction to 4NDMABI, the DMABI doesn't have N atom lone-pair as center for hydrogen bond formation with solvent and can be used as a reference for zero acidity.



DMABI



4NDMABI

If that assumption is true, the linear relationship between the maximum wavenumbers of lowest energy absorption bands of the DMABI and 4NDMABI in solvents with $\alpha \approx 0$ should exist. As shown in Fig. 2, good correlation (R^2 = 0.998) of experimental values exist, including results for aromatic (toluene) and polychlorinated aliphatic (tetrachloromethane) solvents. If one's use the obtained equation

$$\upsilon \text{ (4NDMABI)} = 0{,}948 \; \upsilon \text{ (DMABI)} + 365 \text{ cm}^{-1},$$

the maximum wavenumbers for 4NDMABI excluding the hydrogen bond influence can be calculated (Table 1).

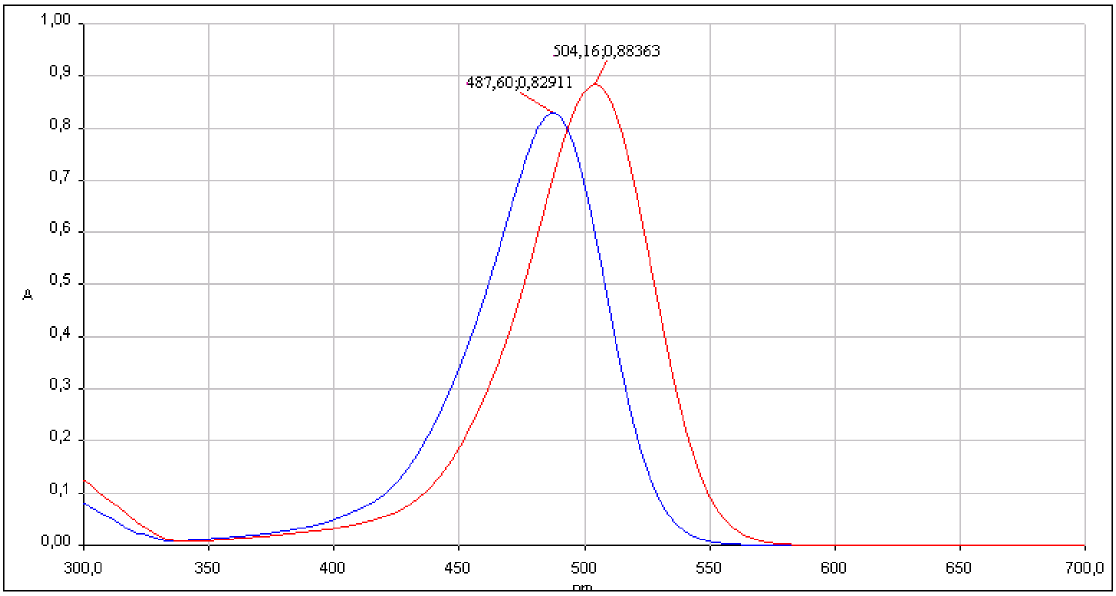


Fig. 1. *UV-vis absorption spectra of DMABI and 4NDMABI in ethanol.l l=1,0 cm.*

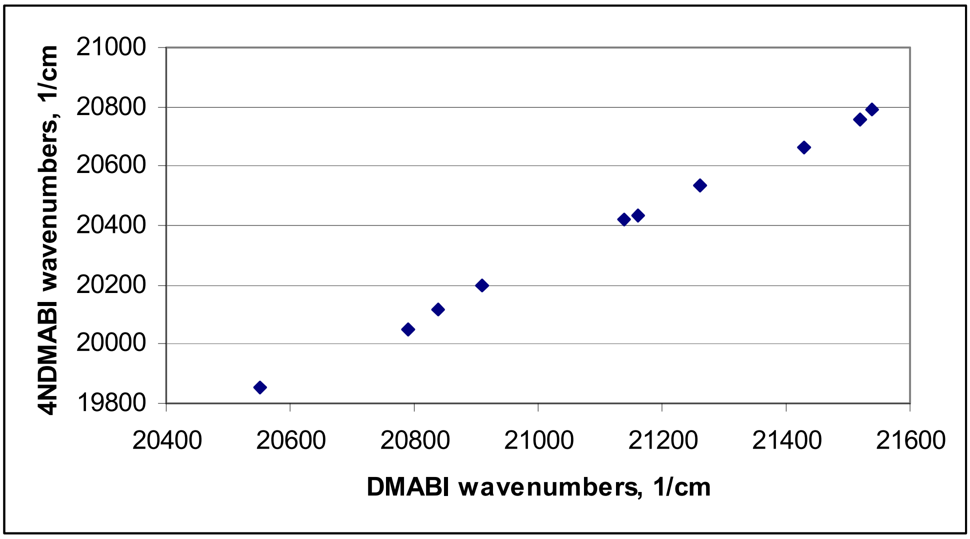


Fig. 2. *Correlations between maximum wavenumbers of lowest energy absorption bands of the DMABI and 4NDMABI in solvents: tetrachloromethane, toluene, 1,4-dioxane, methyl t-butyl ether, diethyl ether, ethyl benzoate, ethyl acetate, acetone, N,N-dimethylformamide, acetonitrile (from left to right)*

Like the Kamlet –Taft α values the difference between calculated an experimental maximum wavenumbers (Δ 4NDMABI) will show the hydrogen donor ability of the solvent.

Accordingly to the Table and Fig.3 both rows of independent characteristics are corresponding, but the Δ 4NDMABI values don't be in good harmony with the Kamlet –Taft α values in the lower value region.

Table 1

Solvatochromic effects and characteristics of solvents

Solvent	Maximum wavenumbers, cm^{-1}				α [3]
	DMABI Experim.	4NDMABI Experim.	4NDMABI Calcul.	Δ 4NDMABI	
Tetrachloromethane	21430	20660	20682	22	0
Toluene	21140	20421	20407	-14	0
1,4-Dioxane	21260	20535	20520	-15	0
Methyl t-butyl ether	21520	20760	20767	7	0
Diethyl ether	21540	20790	20786	-4	0
Ethyl benzoate	20790	20050	20075	25	0
Ethyl acetate	21160	20437	20426	-11	0
Acetone	20910	20197	20189	-8	0.08
N,N-dimethylformamide	20550	19853	19847	-6	0
Acetonitrile	20840	20116	20122	6	0.19
Acetylacetone	20700	19976	19989	13	-
Nitromethane	20647	19890	19939	49	0.22
Methanol	20630	19780	19923	143	0.93
Methanol-d_1	20680	19830	19971	141	-
Acetic acid	20576	19669	19872	203	1.12

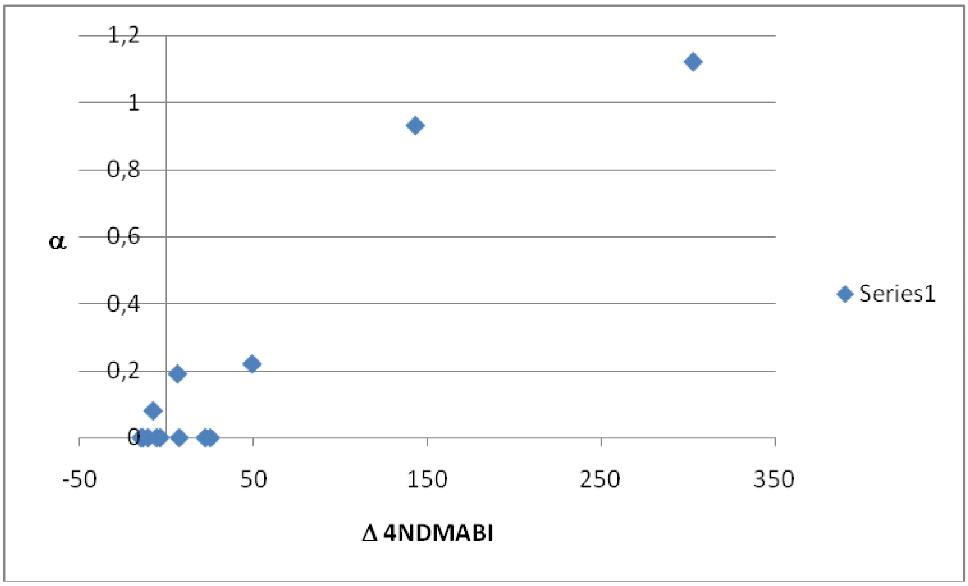


Fig.3. *Interconnection between Δ 4NDMABI and Kamlet –Taft α values. R=0,946.*

Accordingly to our results acetone and also acetonitrile as solvents don't show H-donor ability. Nitromethane, methanol and acetic acid show remarkable H-donor ability and obtained numerical characteristics harmonize with Kamlet –Taft α values. Accordingly to our results methanol and deuteromethanol have the same H- bond donor ability.

Conclusions

Comparison of solvatochromic characteristic of 2-(4'-N,N-dimethylaminobenzylidene-1,3-indandione and 4-aza-2-(4'-N,N-dimethylaminobenzylidene-1,3-indandione allow to obtain new independent characteristic of solvent H-bond donor properties. Accordingly to them acetone, acetonitrile and acetylacetone as solvents don't have H-donor ability. Opposite to them nitromethane, methanol and acetic acid H-donor ability is remarkable and fit in Kamlet –Taft α values. Methanol and deuteromethanol have the same H- bond donor properties.

Acknowledgements

Thanks are due to Latvian Council of Science for financial support of project 05.00.26.

References

1. T.Bevilaqua, T.F.Goncales, C.de G.Venturini, V.G.Machado. Solute-solvent and solvent-solvent interactions in the preferential solvation of 4-[4-(dimethylaminp0styryl]-1-methylpyridinium iodide in 24 binary solvent mixtures. Spectrochimica Acta PartA, 2006, 65, 535-542
2. M.Karelson in Handbook of solvents, ed.G Wypych, Chem Tec Publishing, 2001, 639-682
3. M.J.Kamlet, J.M.Abboud, M.H.Abracham, R.W.Taft. Linear solvation energy relationships. 23. A comprehensive collection of the solvatochromic parameters π*, α, and β, and some methods for simplifying the generalized Solvatochromic Equation. J.Org.Chem., 1983, 48, 2877-2887
4. K. A. Bello, L. Cheng, J. Griffiths. Near-infrared absorbing methine dyes based on dicyanovinyl derivatives of indane-1,3- dione *J. Chem. Soc. Perkin Trans. 2*, **6**, 815 (1987)
5. Neilands, O., Muzikante, I. (2003), in "Organic Nanophotonics, Proceedings of the NATO Advanced Workshop", NATO Science Series II, Vol.100, Kluwer Academic Publishers, pp.447-462

V.Kampars, P.Pastors. Solventu raksturojumu noteikšana salīdzinot 4-aza-2-(4'-dimetilaminobenziliden)-1,3-indandiona un 2-(4'-dimetilaminobenziliden)-1,3-indandionasolvatohromiju.

Ar mērķi iegūt jaunu informāciju par šķīdinātāju spēju veidot H-saites ar izšķīdināto vielu salīdzināta 2-(4'-N,N-dimetilaminobenziliden)-1,3-indandiona (DMABI) un 4-aza-2-(4'-N,N-dimetilaminobeniliden)-1,3-indandion (4NDMABI) solvatohromija. Šķīdinātājos, kuros H-saites radītā stabilizācija ir nenozīmīga, eksistē lineāra sakarība: υ (4NDMABI) = 0,948 υ (DMABI) + 365 cm^{-1}, R^2= 0.998. Izmantojot šo vienādojumu var aprēķināt 4NDMABI hipotētisko garo viļņu absorbcijas joslas viļņu skaitli pārējos šķīdinātājos. Salīdzinot aprēķinātos un eksperimentālos lielumus var spriest par šķīdinātāja H-donorajām īpašībām. No pētītajiem šķīdinātājiem tikai nitrometāns, metanols, deiterometanols un etiķskābe ir šķīdinātāji, kuri veido pietiekami efektīvas H-saites ar 4NDMABI nedalīto elektronu pāri. H-donorās īpašības pieaug virzoties no nitrometāna uz etiķskābi. Metanola un deiterometanola H-donorās īpašības ir praktiski vienādas.

Kampars V., Pastors P. Determination of solvents characteristics by comparison the 4-aza-2-(4'-N,N-dimetilaminobenziliden)-1,3-indandione and 2-(4'-N,N-dimetilaminobenziliden)-1,3-indandione solvatochromy.

With the purpose to obtain new information about the ability of solvents to form H-bond with the dissolved substance it is compared UV-Vis spectra of the 4-aza-2-(4'-N,N-dimetilaminobenziliden)-1,3-indandione (4 4NDMABI) and 2-(4'-N,N-dimetilaminobenziliden)-1,3-indandione (DMABI). In solvents with the insignificant H-bond ability there is a linear regularity: υ (4NDMABI) = 0,948 υ (DMABI) + 365 cm^{-1}, R^2= 0.998. Using this equation it is possible to calculate the hypothetical wave number of long-wave absorption band (4NDMABI) in solvents with H-bond ability. From the investigated solvents only nitromethane, methanol, deuteromethanol and acetic acid form effective H-bond with the unshared electronic pair 4NDMABI. H-donor ability grows in the direction from the nitromethane to acetic acid (49, 143, 141, 203). The H-donor ability of methanol and deuteromethanol is practically equal.

Кампарс В., Пасторс П. Определение характеристик растворителей сравнением сольватохромии 4-аза-3-(4'-N,N-диметиламинобензилиден)-1,3-идадиона и 2-(4-'N,N-диметиламинобензилиден)-1,3-идадиона.

С целью получение новой информации о способности растворителей образовать Н-связи с растворенным веществом сравнена сольватохромия 4-аза-3-(4'-N,N-диметиламинобензилиден)-1,3-идадиона (4NDMABI) и 2-(4'-N,N-диметиламинобензилиден)-1,3-идадиона (DMABI). В растворителях с незначительной Н-связью вызванной стабилизацией существует линеарная закономерность: υ (4 NДМАБИ) = 0,948 υ (DMABI) + 365 cm^{-1}, R^2= 0.998. Применяя это уравнение можно рассчитать гипотетическое волновое число длинноволновой полосы поглощения (4NDMABI) в остальных растворителях. Сравнением расчетных и экспериментальных данных, можно судить о Н-донорных свойствах примененного растворителя. Из исследованных растворителей только нитрометан, метанол, дейтерометанол и уксусня кислота образуют достаточно эффективные Н-связи с неподеленной электронной парой 4NDMABI. Н-донорные свойства возрастают в направлении от нитрометана к уксусной кислоте. Н-донорные свойства метанола и дейтерометанола практически не отличаются.