JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 9, 459–470 (1996)

SOLVENT EFFECTS ON AROMATIC NUCLEOPHILIC SUBSTITUTIONS. PART 6. KINETICS OF THE REACTION OF 1-CHLORO-2, 4-DINITROBENZENE WITH PIPERIDINE IN BINARY SOLVENT MIXTURES†

P. M. E. MANCINI*†, A. TERENZANI†, M. G. GASPARRI†§ AND L. R.VOTTERO†

†Departamento de Química Orgánica, Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, (3000) Santa Fe, República Argentina

§Instituto de Investigaciones de Productos Naturales, de Análisis y Síntesis Orgánica (IPNAYS), CONICET, UNL, Santiago del Estero 2829, (3000) Santa Fe, República Argentina

The kinetics of the reaction between 1-chloro-2,4-dinitrobenzene and piperidine was studied in several completely non-aqueous binary solvent mixtures where the preferential solvation is the rule at 15, 25 and 40 °C. The reaction was chosen as the simplest example of aromatic nucleophilic substitutions (ANS). For (aprotic solvent + aprotic co-solvent) binary systems the co-solvent was toluene, and the rest of the solvents used were selected with different structural characteristics and an extensive range of polarity. In this kind of mixture a property of mixed binary solvents would be defined by means of $E_T(30)$ values and the solvent effects on this simple model of ANS reactions are similar to those of aprotic pure solvents, especially if hydrogen-bond donor solvent mixtures are excluded from the analysis. For (aprotic solvent + protic co-solvent) binary systems the co-solvent used was methanol. The presence of a protic solvent in the mixture strongly determines the solvent effects on the reaction. In this type of binary mixture, the chemical probe under consideration may not be generally valid to interpret solvation effects. Additionally, empirical solvent polarity parameters $E_T(30)$ were determined UV–VIS spectrophotometrically for some pure aprotic solvents and, as a function of the composition, for (dimethylformamide + toluene), (toluene + methanol) and (1,1,1-trichloroethane + methanol) at 15 and 40 °C, with the purpose of extending the studies on the empirical polarity indices in binary solvent mixtures to the thermo-solvatochromic area.

INTRODUCTION

The considerable significance that solvents have in chemical and physical processes has frequently been pointed out in the recent literature.[1,2] Chemists have usually attempted to understand solvent effects in terms of *polarity*, which, in a broad sense, relates to the overall solvating capability of a solvent. Numerous reports on solvent polarity scales have been published in the last few decades. These scales have been designed on single and multiple parameter approaches and they are mainly derived from spectroscopic measurements.[3–5] More recently, Abraham[6] devised scales of solute hydrogen-bond acidity and solute hydrogen-bond basicity, and have devised a general solvation equation.

The reactivity of aromatic nucleophilic substitution (ANS) reactions is notably affected by the solvent polarity. Since the first pioneering studies,[7] different contributions have been reported to show how extensive and complex are the interactions of the substrate and/or the intermediate(s) with the solvent molecules.[8] In addition to the non-specific coulombic, inductive and dispersion interactions, others such as specific hydrogen-bond, electron-pair donor (EPD)/electron-pair acceptor (EPA) and solvophobic interactions may all play a part.[9]

For the reactions of nitroaryl halides with either primary or secondary amines, the two-step mechanism shown in Scheme 1 is fully established: the breakdown of the zwitterionic σ intermediate, ZH, can occur spontaneously

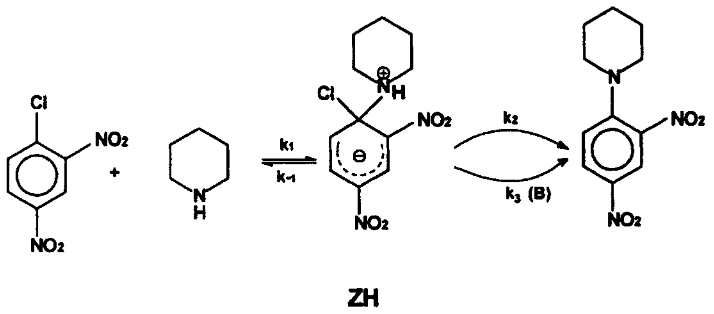
---

[*] Author to whom correspondence should be addressed.

[†] Presented in part at the XX Congreso Argentino de Química, Córdoba, Argentina 1994.

CCC 0894–3230/96/070459–12

Received 8 August 1995
Revised 9 February 1996



Scheme 1

or by a base-catalyzed mechanism. The transition state leading to the ZH intermediate is expected to be favored by increasing solvent polarity. Particularly detailed studies have been carried out with one of the simplest systems of ANS: the reaction of 1-chloro-2,4-dinitrobenzene (2,4-DNCB) with piperidine (PIP). In connection with this, we have studied the influence of solvent effects on the reaction rate in 13 aprotic solvents with a dielectric constant range of 43 units,[10] showing that kinetic data are well correlated by the Dimroth–Reichardt solvent polarity scale $E_T(30)$. The correlation is remarkably good ($r>0{\cdot}98$) if hydrogen-bond donor (HBD) solvents are excluded. For hydroxylic solvents, which exhibit highly specific properties (inter- or intramolecular hydrogen bonding, acidity and basicity and self-association), the reactivity was inversely proportional to the hydrogen-bond donating ability of the solvents.[11] The solvent effects of alkanols are satisfactorily correlated by Taft's polar substituent constant σ^*[12] ($r=0{\cdot}99$). Moreover, we have detected that the reaction rate in these hydroxylic solvents is smaller than that observed in cyclohexane (the slowest in the aprotic solvent series), which suggests that inter- and intramolecular bond interactions, in the pure solvent and between the solvent and the amine, are relevant in determining the reaction rates.[13]

Solvent effects in ANS involving nitrohalobenzenes with amines were reported in the 1960s, including mixed solvents, and the reaction of 2,4-DNCB with PIP mainly in binary aqueous–organic mixtures.[7b,14] We have now explored the kinetic behavior of the above reaction in a variety of completely non-aqueous binary mixtures of solvents. The object of this work was to supplement a systematic study of the solvent influence on this simple model of the ANS reaction. It was aimed at determining the second-order rate coefficients depending on the nature and concentration of the solvent and the possible interactions in binary mixtures.

Solute–solvent interactions are more complex in mixed solvents than in pure solvents owing to the possibility of preferential solvation,[15] which is important to explain spectroscopic, equilibrium and kinetic results in binary mixtures.

The chemical characteristics of solvent mixtures are customarily determined in the same manner as those of neat solvents by means of chemical probes.[16] We have recently reported $E_T(30)$ values at 25 °C for several binary solvent systems showing that the change in this polarity parameter is not only a function of the relative concentration of the solvent but also of the chemical nature of the mixed components.[17] Therefore, it was of interest to correlate the kinetic data with $E_T(30)$ values in order to evaluate the influence of the preferential solvation. We have also determined $E_T(30)$ values for several aprotic solvents and for some binary solvent systems at 15 and 40 °C with the purpose of including the thermo-solvatochromism phenomenon in the discussion.

RESULTS AND DISCUSSION

Kinetic studies

The kinetics of the reaction between 2,4-DNCB and PIP was studied in two different models of completely non-aqueous binary mixtures. A co-solvent (Co) consisting of a compound with particular characteristics was chosen in each model, which was common and took part in the different mixtures studied. Each binary solvent mixture was explored at different compositions. The types of binary solvent mixtures used were as follows:

(ApS_i + ApCo):	binary mixtures of an aprotic solvent (ApS) and the aprotic co-solvent (ApCo);
(ApS_i + PCo):	binary mixtures of an aprotic solvent (ApS) and the protic co-solvent (PCo):

Kinetics of the reaction of 1-chloro-2,4-dinitrobenzene with piperidine in (ApS_i + ApCo) solvent systems

Toluene was chosen as co-solvent owing to its character as a non-hydrogen-bonding (NHB) aromatic solvent. All other solvents were selected with different structural properties and a large range of polarity: chloroform, 1,4-dioxane, ethyl acetate, tetrahydrofuran (THF), acetone, nitromethane and *N*,*N*-dimethylformamide (DMF). Chloroform and nitromethane were taken as examples of HBD solvents and the others were included as hydrogen-bond acceptor (HBA) solvents.

Although *a priori* no base catalysis was expected for the nucleofuge chloride, the influence of amine concentration on the reaction rate was studied. In all cases the reactions were carried out under pseudo-first-order conditions; they yielded the expected *N*-(2,4-dinitrophenyl)piperidine in quantitative yield, and proved to be first order in substrate. The second-order rate coefficients, k_A, calculated from the experimental pseudo-first-order rate coefficients, k_φ, are listed in Table 1 for the reactions at 25 °C. The reactions in the (DMF + Toluene) solvent system, which were previously studied at 25 °C,[17] were additionally examined at 15 and 40 °C. The kinetic data are given in Table 2. The kinetic data show a general tendency of a decrease in k_A values with increase in co-solvent concentration due to the decrease in the overall solvation capability of the solvent mixture.

Table 1. Second-order rate coefficients, k_A, for the reaction of 1-chloro-2,4-dinitrobenzene (**I**) with piperidine in (ApS_i + ApCo) at 25 °C[a]

	[Piperidine]/M			
Solvent	0·040	0·080	0·160	0·250
(Chloroform + toluene)				
0·10	8·70	8·64	8·79	8·60
0·30	8·38	8·31	8·44	8·45
0·50	7·24	7·25	7·23	7·29
0·70	6·95	6·88	7·04	7·06
0·90	6·72	6·79	6·83	6·86
(1,4-Dioxane + toluene)				
0·10	11·9	11·2	12·0	12·3
0·30	11·5	11·7	11·1	10·7
0·50	10·9	11·1	10·8	11·3
0·70	10·1	9·52	10·2	10·5
0·90	8·24	8·22	8·23	8·29
(Ethyl acetate + toluene)				
0·10	23·4	23·3	23·8	23·7
0·30	22·3	22·2	22·6	22·2
0·50	17·6	17·5	17·9	17·4
0·70	15·5	15·3	15·8	15·7
0·90	12·1	12·3	12·9	12·5
(THF + toluene)				
0·10	29·0	29·3	29·4	29·6
0·30	27·9	28·0	28·6	27·1
0·50	21·5	21·9	21·9	21·7
0·70	16·2	17·1	16·4	16·8
0·90	10·0	9·68	10·2	10·4
(Acetone + toluene)				
0·10	50·4	50·2	49·1	49·8
0·30	42·3	42·4	43·5	42·9
0·50	35·1	35·7	36·3	35·9
0·70	26·3	25·4	24·8	25·8
0·90	18·4	18·8	19·5	19·1
(Nitromethane + toluene)				
0·10	68·8	69·6	68·7	69·3
0·30	48·1	50·5	50·9	49·5
0·50	38·5	36·9	39·8	38·4
0·70	30·8	30·5	29·5	30·1
0·90	18·3	18·1	17·7	17·8

[a] [**I**] = 10^{-4} M; values of $10^2 k_A$/l mol^{-1} s^{-1}; the concentrations of the binary mixtures are in mole fraction of toluene.

Kinetics of the reaction of 1-chloro-2,4-dinitrobenzene with piperidine in (ApS_i + PCo) solvent systems

The co-solvent selected in this type of binary solvent system was methanol, which is known to form strong hydrogen bonds and is capable of acting as an HBD–HBA solvent. Among the alkanols, methanol exhibits the largest self-association energy ($\delta_{SA} = 3{\cdot}0$)[18] and acidity ($\alpha = 1{\cdot}09$)[19] values with an excellent correlation between the extent of oligomerization and HBD ability. The rest of the solvents used were toluene, chloroform, 1,1,1-trichloroethane (1,1,1-TClE), THF, acetone, DMF and dimethyl sulfoxide (DMSO).

We have recently reported the second-order-rate coefficients, k_A, for the present reaction in (1,1,1-TClE + methanol) mixtures at 25 °C.[17] Consequently, the reactions carried out in (1,1,1-TClE + methanol) were examined at 15 and 40 °C. Additionally, the reactions in (toluene + methanol) mixtures were studied at three temperatures (15, 25 and 40 °C). Table 3 lists the second-order rate coefficients, k_A, and the calculated activation parameters where it can be seen that no significant rate acceleration occurs on increasing the amount of amine, similarly to the previous results in (1,1,1-TClE + methanol) at 25 °C. The reactions performed in the other binary solvent systems were examined at only one temperature (25 °C). The kinetic data are presented in Table 4. A slight acceleration in reaction rates was verified in those mixtures where the aprotic solvent is less polar and, especially, in the binary mixtures with a lower concentration of the protic co-solvent. According to Bunnett and Garst's[20] criterion and Bernasconi *et al.*'s[21] alternative criterion, this phenomenon cannot be considered as base catalysis. In addition, it was seen that for (toluene + methanol) mixtures the k_3/k_2 ratio decreases with increase in temperature. A possible explanation for the observed acceleration would be a solvation effect. This interpretation would be in accordance with previous results corresponding to reactions carried out in pure solvents.[10b]

On the other hand, the kinetic values shown in Tables 3 and 4 exhibit an initially very important decrease in k_A values with small increments in methanol concentration. Several years ago it was demonstrated that when a substrate has an *o*-nitro group the addition of a small

Table 2. Second-order rate coefficients, k_A, for the reaction of 1-chloro-2,4-dinitrobenzene (I) with piperidine in (*N*,*N*-dimethylformamide + toluene) binary solvent mixtures at 15 and 40 °C.[a]

	[Piperidine]/M							
	15 °C				40 °C			
X_{TOL}	0·04	0·08	0·16	0·25	0·04	0·08	0·16	0·25
0·10	76·6	76·7	77·7	75·9	154	155	149	158
0·30					129	122	120	128
0·50	60·0	59·8	63·1	62·5	116	107	118	120
0·70	32·3	45·3	38·1	41·0	102	99	109	111
0·90	18·3	18·0	18·1	17·8	42·8	41·5	41·7	42·9

[a] [I] = 10^{-4} M; values of $10^2 k_A$/l mol^{-1} s^{-1}

Table 3. Second-order rate coefficients, k_A, for the reaction of 1-chloro-2,4-dinitrobenzene (I) with piperidine in (1,1,1-TClE + methanol) and (toluene + methanol) binary solvent mixtures at 15 and 40 °C, and the activation parameters[a]

	[Piperidine]/M									
	15 °C				40 °C					
Solvent	0·04	0·08	0·16	0·25	0·04	0·08	0·16	0·25	ΔH^{*}/kJ mol^{-1}	$-\Delta S^{*}$/J mol^{-1} K^{-1}
(1,1,1-TClE + methanol)										
0·10	2·49	2·50	2·86	3·29	9·09	8·83	9·90	11·3	34·7	153·5
0·30	1·20	1·32	1·61	1·72	4·58	4·74	5·03	5·28	33·0	152·8
0·50	0·96	1·04	1·14	1·35	3·60	3·80	3·93	4·37	34·3	175·6
0·70	0·830	0·950	1·04	1·15	3·40	3·55	3·62	3·95	34·9	174·6
0·90	0·686	0·728	0·800	0·827	3·20	3·15	3·08	3·86	42·4	151·5
(Toluene + methanol)										
0·10	0·912	1·14	1·47	2·03	6·24	6·51	7·10	7·69	43·6	123·1
0·30	0·631	0·677	0·760	0·872	3·48	3·54	3·73	4·09	45·2	125·8
0·50	0·610	0·588	0·625	0·720	3·17	3·29	3·45	3·62	47·4	113·3
0·70	0·621	0·651	0·683	0·708	3·19	3·26	3·25	3·30	44·8	130·2
0·90	0·693	0·698	0·703	0·705	2·96	2·91	3·05	3·08	41·1	142·9

[a] [I] = 10^{-4} M; values of $10^2 k_A$/l mol^{-1} s^{-1}; the concentrations of the binary mixtures are in mole fraction of methanol.

amount of an HBD solvent to an aprotic solvent produces an important decrease in rate.[14–c]

The strikingly low reactivity previously observed for reactions in alkanols must be associated with a specific hydroxylic solvent effect on this system.[11] In the presence of piperidine, alcohols are known to act as hydrogen-bond donors, and there is abundant evidence of strong hydrogen-bonding interactions between piperidine and methanol.[22] Piperidine is considered to be a solute with a constant overall hydrogen-bond basicity ($\Sigma \beta^{H}_{2} = 0{\cdot}69$).[6] In the case of the reactions developed in (toluene + methanol) and (1,1,1-TClE + methanol) the activation parameters are also consistent with the rationale of hydrogen bonding causing the decrease in the rates: these reactions exhibit enthalpies and entropies of activation comparable to those corresponding to the reaction carried out in pure methanol.

It is well known that for the reaction of *o*- and *p*-nitrohalobenzenes with amines, the magnitude of the $k_{ortho}:k_{para}$ ratio is strongly solvent dependent and the 'built-in solvation' plays an important part.[7a,14d,e] The presence of the protic solvent as part of the binary mixture would produce changes in the amine and in the intermediate state solvation models. The extent of differential solvation depends on the intermolecular forces between the solute and surrounding solvent molecules. The sensitivity of the reaction rate toward the small amount of methanol could be explained as a change in the solvation of ZH due to the competition between the 'built-in solvation' and the specific solvation from the co-solvent with a special distribution in the rest of the mixture. Subsequent increases in methanol concentration should only modify the whole solvent mixture, remaining relatively constant

Table 4. Second-order rate coefficients, k_A, for the reaction of 1-chloro-2,4-dinitrobenzene (**I**) with piperidine in (ApS_i + PCo) at 25 °C[a]

	[Piperidine]/M		
Solvent	0·080	0·160	0·250
(Toluene + methanol)			
0·10	2·06	2·73	3·48
0·30	1·46	1·72	1·93
0·50	1·18	1·42	1·57
0·70	1·21	1·38	1·43
0·90	1·37	1·41	1·42
(Chloroform + methanol)			
0·10	2·83	3·18	3·45
0·30	2·29	2·32	2·14
0·50	1·64	2·08	1·77
0·70	1·80	1·78	1·83
0·90	1·71	1·74	1·71
(THF + methanol)			
0·10	18·3	18·7	18·9
0·30	9·47	9·78	9·81
0·50	5·33	5·83	5·63
0·70	3·24	3·63	3·70
0·90	2·26	2·20	2·30
(Acetone + methanol)			
0·10	29·1	29·9	30·3
0·30	14·5	13·8	14·9
0·50	6·06	6·10	6·14
0·70	3·47	3·72	3·66
0·90	2·71	2·70	2·76
(DMF + methanol)			
0·10	90·0	85·3	91·5
0·30	43·1	44·5	41·5
0·50	19·0	20·1	20·6
0·70	8·05	7·84	8·10
0·90	3·33	3·43	3·44
(DMSO + methanol)			
0·10	151	156	152
0·30	92·8	91·7	92·1
0·50	38·3	39·3	40·0
0·70	13·3	13·1	12·8
0·90	3·53	3·63	3·61

[a] [I] = 10^{-4} M; values of $10^2 k_A$/l $mol^{-1} s^{-1}$; the concentrations of the binary mixtures are in mole fraction of methanol.

around ZH. The influence of methanol is more significant on its binary mixtures with the aprotic less polar solvents. With the (toluene + methanol), (chloroform + methanol) and (1,1,1-TClE + methanol) solvent systems, a decrease of 50% in the reaction rate can be observed with respect to the values corresponding to the pure aprotic solvent with only $X_{MeOH} \approx 0{\cdot}05$ in the mixtures. For the rest of the binary systems explored, $X_{MeOH} \approx 0{\cdot}15$ is necessary to produce the same effect.

Correlation analysis

It is possible to interpret the solvent effects with the aid of model processes that yield the same or similar effects. In connection with this, several spectroscopically based single parameters have been used to establish empirical scales of solvent polarity (single parameter approaches).[23] These scales are supported on convenient, well known, easily measurable, solvent-sensitive reference processes within the framework of linear-free energy relationships (LFE).[24–26] The use of individual solvent parameters to predict solvent effects should be limited in a first approach to largely analogous processes.

Negatively and positively solvatochromic dyes are particularly suitable as standard substances for the determination of empirical solvent parameters and, of these, by virtue of the exceptionally large extent of its solvatochromism, the negatively solvatochromic 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt's betaine dye) is especially suitable.[9a] The Dimroth–Reichardt $E_T(30)$ scale is one of the most comprehensive ones among the single-parameter approaches.[27] This polarity index measures different combinations of the ability of a solvent to donate a hydrogen atom towards the formation of a hydrogen bond and its actual polarity and polarizability.

As mentioned in the Introduction, we have recently determined by UV–VIS spectrophotometry empirical solvent polarity parameters $E_T(30)$ for different (ApS_i + toluene) and (ApS_i + methanol) solvent systems as a function of composition. A preliminary application of these empirical parameters was discussed with the aid of two examples related to the solvents effects on the reaction of 2,4-DNCB with PIP carried out in (DMF + toluene) and (1,1,1-TClE + methanol), respectively.[17] In each case a satisfactory correlation was found between $E_T(30)$ values and the logarithms of rate constants.

In a neat solvent, all solutes have the same environment; therefore, a solvent property should be generally valid. In solvent mixtures when preferential solvation is operative the chemical probe has in its environment more of one solvent than of the other, compared with the bulk composition. Preferential solvation of the chemical probes plays a dominant role in determining the size of parameters measured by them in solvent mixtures.[16a,28] We observed only one case among the many mixtures cited in our previous paper[17] where preferential solvation does not take place: the $E_T(30)$ of (dioxane + toluene) is strictly linear with the solvent composition. In the other cases explored we detected preferential solvation. Recently, Bosch and coworkers[15,29] proposed theoretical equations that allow numerical descriptions of the preferential solvation in binary mixtures, which can be related to the spectroscopic shifts in the $E_T(30)$ solvatochromic indicator and dissociation constants of electrolytes.

Considering that preferential solvation of the $E_T(30)$ betaine in mixtures of solvents is the rule, we extended the preceding correlation analysis between $E_T(30)$ values and the logarithms of the rate constant at 25 °C to each of the (ApS_i + toluene) and (ApS_i + methanol) systems. The kinetic studies of the present reaction were performed with that purpose. The correlations were assessed by the evaluation of the correlation coefficients (r) and the standard deviations (s). The results are presented in Tables 5 and 6. The regression equations summarized in Table 5 are reasonably good for (ethyl acetate + toluene), (THF + toluene), (acetone + toluene) and (nitromethane + toluene), with correlation coefficients ranging from 0·986 to 0·999 and standard deviations from 0·018 to 0·056 in the same form as previous results for (DMF + toluene). However, the correlations are poor for (chloroform + toluene) and (1,4-dioxane + toluene). In the first case the regression improves if the data corresponding to high X_{TOL} are eliminated. The behavior of the (1,4-dioxane + toluene) mixture is surprising because the system exhibits a decrease in $E_T(30)$ values as a linear function of co-solvent mole fraction, suggesting additivity.[30,31]

In general, the typical $E_T(30)$ vs X_{TOL} curves observed for (ApS_i + toluene) systems are consistent with binary mixtures of a non-associated component which does not interact with the associated component, but only dilutes it. This is the case for those binary systems[17] which show the best regression equations.

The correlation analysis shown in Table 6 indicates that the regression equations for (toluene + methanol) and (chloroform + methanol) are relatively good (r>0·95; s<0·090), similarly to previous results observed for (1,1,1-TClE + methanol). The regression equations corresponding to (THF + methanol), (acetone + methanol), (DMF + methanol) and (DMSO + methanol) are poor (r = 0·92–0·94; s = 0·190–0·315). Except for (DMF + methanol) and (DMSO + methanol), in which the $E_T(30)$ vs X_{MeOH} curves present a continuous non-linear increase as a function of $E_T(30)$ and smaller deviations from additivity, in the rest of the (ApS_i + methanol) systems at low methanol concentration we observed a large increase in $E_T(30)$ values for small increases in co-solvent concentration. In these cases the $E_T(30)$ vs X_{MeOH} curves show an inflection zone that agrees with the longest deviation

Table 5. Correlation coefficient (r), standard error of the estimate (s), slope (q) and intercept (p) and their standard errors (s_q, s_p) and the number of data points (n) for log k_A vs $E_T(30)$ in the (ApS_i + toluene) system at 25 °C[a]

Solvent	r	s	q	s_q	p	s_p	n
(Chloroform + toluene)	0·844	0·030	0·023	$6{\cdot}62 \times 10^{-3}$	−1·992	0·249	7
Except for: $X_{TOL} = 1$	0·927	0·021	0·042	$8{\cdot}60 \times 10^{-3}$	−2·733	0·328	6
Except for: $X_{TOL} = 0{\cdot}90, 1$	0·959	0·015	0·060	$1{\cdot}03 \times 10^{-2}$	−3·436	0·398	5
(1,4-Dioxane + toluene)	0·863	0·051	0·096	$2{\cdot}52 \times 10^{-2}$	−4·371	0·883	7
Except for: $X_{TOL} = 0$	0·909	0·045	0·119	$2{\cdot}70 \times 10^{-2}$	−5·157	0·947	6
Except for: $X_{TOL} = 0, 0{\cdot}1$	0·915	0·046	0·143	$3{\cdot}70 \times 10^{-3}$	−5·993	1·265	5
(Ethyl acetate + toluene)	0·997	0·018	0·141	$5{\cdot}15 \times 10^{-3}$	−5·957	0·186	7
(THF + toluene)	0·987	0·044	0·181	$1{\cdot}30 \times 10^{-2}$	−7·275	0·468	7
(Acetone + toluene)	0·986	0·056	0·108	$8{\cdot}02 \times 10^{-2}$	−4·784	0·315	7
(Nitromethane + toluene)	0·999	0·002	0·086	$1{\cdot}79 \times 10^{-3}$	−4·077	0·075	7

[a] The correlations were calculated for X_{TOL} = 0, 0·10, 0·30, 0·50, 0·70, 0·90 and 1.

Table 6. Correlation coefficient (r), standard error of the estimate (s), slope (q) and intercept (p) and their standard errors (s_q, s_p) and the number of data points (n) for log k_A vs $E_T(30)$ in the (ApS_i + methanol) system at 25 °C.[a]

Solvent	r	s	q	s_q	p	s_p	n
(Toluene + methanol)	0·955	0·084	−0·035	$4{\cdot}86 \times 10^{-3}$	−0·012	0·238	7
(Chloroform + methanol)	0·968	0·073	−0·047	$5{\cdot}40 \times 10^{-3}$	0·687	0·268	7
(THF + methanol)	0·933	0·190	−0·073	$1{\cdot}26 \times 10^{-2}$	2·381	0·625	7
(Acetone + methanol)	0·928	0·231	−0·111	$1{\cdot}98 \times 10^{-2}$	4·572	1·021	7
(DMF + methanol)	0·925	0·299	−0·153	$2{\cdot}81 \times 10^{-2}$	7·061	1·440	7
(DMSO + methanol)	0·937	0·315	−0·193	$3{\cdot}12 \times 10^{-2}$	9·274	1·637	7

[a] The correlations were calculated for X_{MET} = 0, 0·10, 0·30, 0·50, 0·70, 0·90 and 1.

from additivity. Furthermore, in each plot there exists a region where the changes in $E_T(30)$ values are a linear function of the co-solvent concentration owing to the effect of preferential solvation of the methanol–betaine complex from methanol. For co-solvent concentrations higher than $X_{MeOH} = 0\cdot9$ the systems exhibit a tendency to additivity. The three-region concept[32] is especially clear for (toluene + methanol), (chloroform + toluene) and (1,1,1-TClE + methanol)

The regression equations shown in Table 5 present slopes with opposite sign to the slopes of the correlations given in Table 6. This observation clearly indicates different solvation models in the (ApS_i + toluene) and (ApS_i + methanol) binary solvent series.

The next question is to determine if for all the (ApS_i + toluene) binary mixtures under consideration the $E_T(30)$ parameter is available to reflect the experimentally observed solvent effects on the present reaction. In that context we examined (a) the (ApS_i + toluene) binary solvent mixtures studied, at fixed concentrations, and (b) the (ApS_i + toluene) binary solvent mixtures at all concentrations studied, including in this case the data from the literature corresponding to pure aprotic solvents. The regression equations are presented in Table 7. Taking the behavior of aprotic solvents into account, in an attempt to reveal possible trends for different types of (ApS_i + toluene) system, these were grouped into three categories: all mixtures (ALLm), HBA mixtures (HBAm) and HBD mixtures (HBDm).

For each fixed concentration analyzed (toluene molar fraction 0·1, 0·3, 0·5, 0·7 and 0·9), considering all binary mixtures, the correlation between $E_T(30)$ values with the logarithms of the rate constant is poor ($r < 0\cdot90$). However, the regressions are reasonably good if the HBDm are eliminated ($r > 0\cdot95$).

Finally, we examined a possible correlation for all the concentrations studied including 13 aprotic solvents for which the second-order rate coefficients, k_A are known. The statistical results were $r = 0\cdot854$, $s = 0\cdot206$ ($n = 48$). Once again in this case, the correlation between $E_T(30)$ values with the logarithms of the rate constant improve if HBD solvents and HBDm are excluded with $r = 0\cdot973$, $s = 0\cdot090$ ($n = 36$). Figure 1 shows the plot of log k_A versus $E_T(30)$ values corresponding to 13 aprotic solvents and seven (ApS_i + toluene) binary solvent systems.

Thermo-solvatochromism studies

It is known that solvent polarity is temperature dependent. In addition to its negative solvatochromism, pyridinium *N*-phenoxide betaine dyes also exhibit thermo-solvatochromism, piezo-solvatochromism and halochromism phenomena.[2] Measurements of the thermochromism of the betaine dyes have been reported elsewhere.[33]

We now consider empirical solvent polarity parameters $E_T(30)$ for several aprotic solvents and for some binary solvent mixtures at different temperatures. The aprotic solvents and the binary mixtures explored were chosen in connection with the availability of the 2,4-DNCB + PIP reaction kinetic data at 15 and 40 °C. The primary aim of this part of the investigation was to extend the studies on the empirical polarity parameters for binary solvent systems to the thermo-solvatochromic area.

Additional to already available measurements of the thermochromism of *N*-phenolate–pyridinium betaine in different aprotic solvents,[30,31] further measurements were made at 15 and 40 °C. Preliminary measurements

Table 7. The correlation coefficient (r), standard error of the estimate (s), slope (q) and intercept (p) and their standard errors (s_q, s_p) and the number of data points (n) for log k_A vs $E_T(30)$ in the (ApS_i + toluene) system and pure solvents at 25 °C

Solvent	r	s	q	s_q	p	s_p	n
Pure solvents[a] and ALLm at $X_{TOL} = 0\cdot10$	0·842	0·232	0·093	$1\cdot65 \times 10^{-2}$	−4·253	0·662	15
Pure solvents[a] and ALLm at $X_{TOL} = 0\cdot30$	0·824	0·237	0·093	$1\cdot77 \times 10^{-2}$	−4·236	0·702	15
Pure solvents[a] and ALLm at $X_{TOL} = 0\cdot50$	0·825	0·234	0·094	$1\cdot77 \times 10^{-2}$	−4·269	0·697	15
Pure solvents[a] and ALLm at $X_{TOL} = 0\cdot70$	0·843	0·219	0·094	$1\cdot66 \times 10^{-2}$	−4·274	0·646	15
Pure solvents[a] and ALLm at $X_{TOL} = 0\cdot90$	0·862	0·203	0·093	$1\cdot51 \times 10^{-2}$	−4·247	0·579	15
Pure solvents[b] and HBAm at $X_{TOL} = 0\cdot10$	0·961	0·114	0·111	$1\cdot06 \times 10^{-2}$	−4·854	0·417	11
Pure solvents[b] and HBAm at $X_{TOL} = 0\cdot30$	0·957	0·118	0·112	$1\cdot13 \times 10^{-2}$	−4·869	0·438	11
Pure solvents[b] and HBAm at $X_{TOL} = 0\cdot50$	0·962	0·109	0·113	$1\cdot07 \times 10^{-2}$	−4·919	0·412	11
Pure solvents[b] and HBAm at $X_{TOL} = 0\cdot70$	0·964	0·104	0·112	$1\cdot03 \times 10^{-2}$	−4·887	0·392	11
Pure solvents[b] and HBAm at $X_{TOL} = 0\cdot90$	0·959	0·111	0·111	$1\cdot10 \times 10^{-2}$	−4·862	0·412	11
Pure solvents[c] and ALLm	0·854	0·206	0·098	$8\cdot83 \times 10^{-3}$	−4·439	0·341	48
Pure solvents[d] and HBAm	0·973	0·090	0·116	$4\cdot07 \times 10^{-3}$	−5·006	0·178	36

[a] Toluene, chloroform, 1,4-dioxane, ethyl acetate, THF, acetone, nitromethane, DMF.

[b] Toluene, 1,4-dioxane, ethyl acetate, THF, acetone, DMF.

[c] Cyclohexane, toluene, benzene, chloroform, 1,4-dioxane, 1,1,1-TClE, chlorobenzene, ethyl acetate, THF, acetone, nitromethane, DMF, DMSO.

[d] Cyclohexane, toluene, benzene, 1,4-dioxane, 1,1,1-TClE, chlorobenzene, ethyl acetate, THF, acetone, DMF, DMSO.

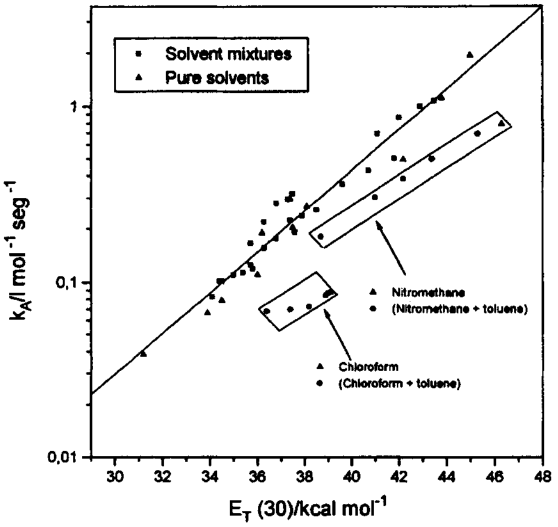


Figure 1. Correlation of log k_A with $E_T(30)$ for the reaction of 1-chloro-2,4-dinitrobenzene with piperidine in (ApS_i + toluene) solvent mixtures (including the pure aprotic solvents) at 25 °C

of $E_T(30)$ values were made in pure aprotic solvents in order to check the determinations by comparing the data obtained with literature data. Table 8, in which values at 25 °C from the literature are included, shows that the $E_T(30)$ values decrease with increase in temperature, which is in agreement with the expected temperature effect.

Binary mixtures of solvents were studied in the second series of measurements. For each temperature

Table 8. $E_T(30)$ values for aprotic solvents at 15, 25 and 40 °C.

Solvent	15 °C	25 °C	40 °C
Cyclohexane		31·2	
Toluene	34·1^c	33·9	33·6^c
Benzene		34·5	
1,4-Dioxane	36·3^b	36·0	35·7^b
1,1,1-TClE	36·9^c	36·2	35·9^c
THF		37·4	
Chlorobenzene	37·6^c	37·5	36·8^c
Ethyl acetate	38·3^c	38·1	37·7^c
Chloroform	41·3^b	39·1	39·9^b
Acetone	42·4^b	42·2	41·7^b
DMF	44·5^c	43·8	43·6^c
DMSO		45·0	44·7^b
Nitromethane	46·6^b	46·3	46·0^b

[a] Data from Ref. 9a.
[b] Values estimated from Ref. 33c.
[c] This work.

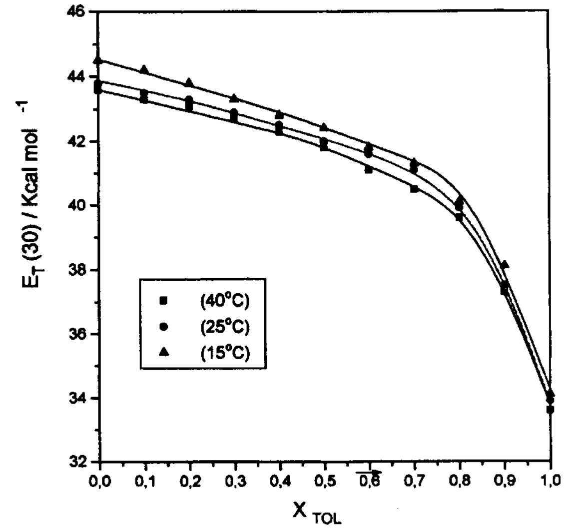


Figure 2: Plot of $E_T(30)$ vs co-solvent mole fraction for (DMF + toluene) solvent mixtures at 15, 25 and 40 °C

indicated we determined the variation of $E_T(30)$ with the composition of the mixtures. Figure 2 shows the shifts in molecular transition energy $E_T(30)$ with increase in toluene concentration for the (DMF + toluene) system at 15, 25 and 40 °C. At each temperature explored, the system exhibits a non-linear decrease in $E_T(30)$ values with increase in co-solvent concentration. An inflection zone is also shown near $X_{TOL} = 0{\cdot}7$, which is in accordance with the largest deviation from additivity. The deviation from linearity is attributed to the preferential solvation of the probe by the solvents of the mixture. The shape of the parameter vs X_{TOL} curve indicates a non-associated component with a low $E_T(30)$ value which does not interact appreciably with the associated component having a relatively high $E_T(30)$ value, but only dilutes it.

On the other hand, Figures 3 and 4 show the shifts in molecular transition energy $E_T(30)$ with increase in methanol concentration for (toluene + methanol) and (1,1,1-TClE + methanol), respectively, at 15, 25, and 40 °C. The plots in Figures 3 and 4 suggest the possible existence of microheterogeneity in such mixtures because the composition of these mixtures may be thought of as consisting of at least three regions. On the ApS_i-rich side, individual methanol molecules interact with individual ApS_i molecules with little disruption of the weak dipole–dipole interaction structure of the main component. The individual methanol molecules which do not participate in the ordinary methanol structure have an HBD ability higher than one that does participate. On the MeOH-rich side, the methanol structure remains more or less intact and the ApS_i molecules are added to cavities in this structure. At intermediate composition, there are clusters of molecules of the same kind, mainly of mutually hydrogen-bonded methanol molecules, surrounded by a region where molecules of the two kinds are near each other. This assumed cluster of methanol has a lower HBD ability than individual molecules of methanol and than methanol molecules in the regular structure. In both cases, it can be seen that the preference for neighbors of the same kind decreases with increasing temperature.

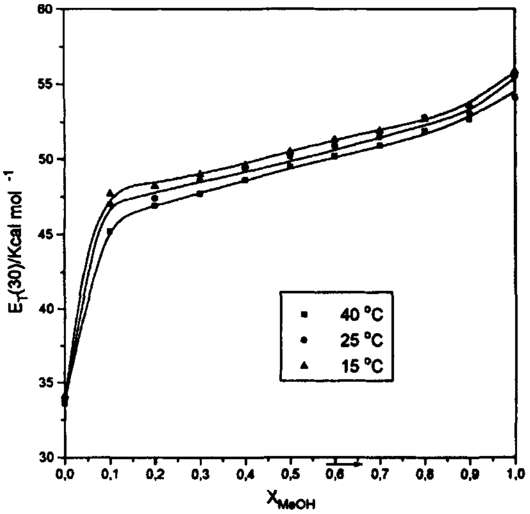


Figure 3: Plot of $E_T(30)$ vs co-solvent mole fraction for (toluene + methanol) solvent mixtures at 15, 25 and 40 °C

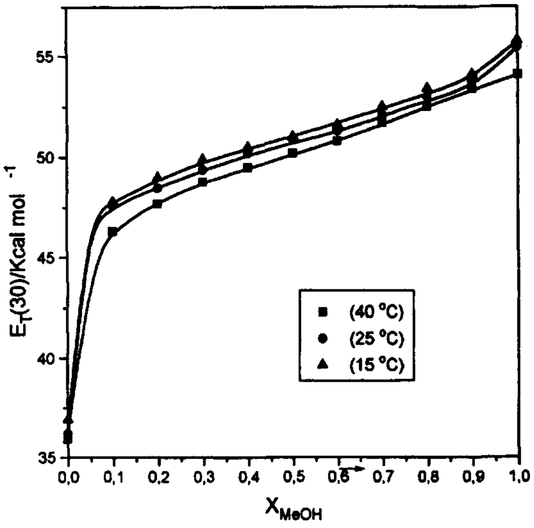


Figure 4: Plot of $E_T(30)$ vs co-solvent mole fraction for (1,1,1-TClE + methanol) solvent mixtures at 15, 25 and 40 °C

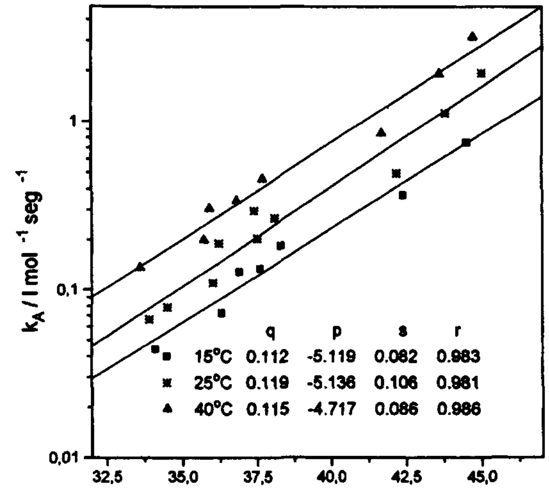


Figure 5: Correlation of log k_A with $E_T(30)$ for the reaction of 1-chloro-2,4-dinitrobenzene with piperidine in pure aprotic solvents at 15, 25 and 40 °C

The relationships found between $E_T(30)$ values and the logarithms of rate constant at 15 and 40 °C, using aprotic solvents alone (DMF, acetone, ethyl acetate, chlorobenzene, 1,1,1-TClE, 1,4-dioxane, toluene and DMSO only at 40 °C) are virtually identical with the relationship previously shown at 25 °C,[10a] as it can be seen in Figure 5, and to the relationship reported in Table 7 for $n = 36$. The series of parallel lines shown in Figure 5 is a result of the present investigation.

On the other hand, similar regression equations at 15 and 40 °C can be observed if the data in Table 2 and Figure 2 corresponding to the (DMF + toluene) solvent system are considered together with the aprotic solvents. The results are shown in Table 9. Additionally, Table 9 presents the correlations for each (toluene + methanol) and (1,1,1-TClE + methanol) binary system

CONCLUSIONS

On the basis of the results obtained from the kinetic and $E_T(30)$ determinations and from the correlation analysis and the thermo-solvatochromic studies, using several binary solvent mixtures, the following conclusions may be drawn.

In the case of completely non-aqueous mixtures of the type (ApS_i + toluene) a 'property of mixed binary solvent' would be defined by means of $E_T(30)$ values. In general, the interactions between the components of binary mixed solvents and the chemical probe is less strong than the self- or mutual-interactions of these components.

Table 9. Correlation coefficient (r), standard error of estimate (s), slope (q) and intercept (p) and their standard errors (s_q, s_p) and the number of data points (n) for log k_A vs $E_T(30)$ at 15 and 40 °C

	15 °C							40 °C						
Solvent mixture	r	s	q	s_q	p	s_p	n	r	s	q	s_q	p	s_p	n
(DMF + toluene)	0·989	0·079	0·119	$8{\cdot}80 \times 10^{-3}$	−5·359	0·360	6[a]	0·990	0·063	0·108	$6{\cdot}96 \times 10^{-3}$	−4·433	0·282	7[c]
(DMF + toluene)	0·982	0·083	0·117	$7{\cdot}55 \times 10^{-3}$	−5·293	0·300	11[b]	0·983	0·077	0·111	$6{\cdot}17 \times 10^{-3}$	−4·566	0·245	13[d]
(Toluene + methanol)	0·923	0·128	−0·040	$7{\cdot}38 \times 10^{-3}$	−0·055	0·365	7[c]	0·972	0·065	−0·036	$3{\cdot}82 \times 10^{-3}$	0·338	0·184	7[c]
(1,1,1-TClE + methanol)	0·987	0·078	−0·069	$5{\cdot}09 \times 10^{-3}$	1·641	0·255	7[c]	0·987	0·064	−0·058	$4{\cdot}18 \times 10^{-3}$	1·580	0·205	7[c]

The correlations were calculated for [a]X_{co} = 0, 0·10, 0·50, 0·70, 0·90 and 1; [b]X_{co} = 0, 0·10, 0·50, 0·70, 0·90 and 1 and 1,4-dioxane, 1,1,1-TClE, chlorobenzene, ethyl acetate, acetone; [c]X_{co} = 0, 0·10, 0·30, 0·50, 0·70, 0·90 and 1; [d]X_{co} = 0, 0·10, 0·30, 0·50, 0·70, 0·90 and 1 and 1,4-dioxane, 1,1,1-TClE, chlorobenzene, ethyl acetate, acetone, DMSO.

The presence of a protic solvent in the mixture determines its characteristics. In all the cases examined the three-region concept would be valid, which is clearer for those mixtures whose aprotic component is less polar. In these cases the reaction rates of this type of ANS reaction have a high sensitivity toward small amounts of the protic solvent in the mixture, and the chemical probe under consideration may not be generally valid to interpret the solvent effects on the reaction.

EXPERIMENTAL

Reagents and solvents. 1-Chloro-2,4-dinitrobenzene and piperidine were purified as described previously.[10a] *N*-(2,4-Dinitrophenyl)piperidine was prepared as reported previously.[10b] 2,6-Diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt's dye, Aldrich, 95%, m.p. 271–275 °C) was used without any further purification. Toluene was kept over sodium wire for several days, refluxed for 72 h and fractionally distilled from sodium (b.p. 110 °C). Anhydrous methanol was prepared by Lund and Bjerrum's method and stored over 3 Å molecular sieves.[34] The rest of the solvents were purified as reported previously and all of them were kept over 4 Å molecular sieves and stored in special vessels that allow delivery without air contamination. All binary solvent mixtures were prepared prior to use and stored under anhydrous conditions.

Kinetic procedures. The kinetics of the reactions were studied spectrophotometrically.[10a] A Perkin-Elmer Model 124 spectrophotometer was used, with a data-acquisition system based on a microprocessor. This set-up has a 12-bit analog-to-digital converter which allows absorbance measurements with an error <0·1% at a maximum rate of 12 readings per second. The microprocessor controls data acquisition, and also measures time through a quartz crystal-controller oscillator. Once data acquisition is completed, data can be read in the system display and/or transferred to a computer through an RS 232-C interface. In all cases, pseudo-first-order kinetics were observed.

Standard solutions of 1-chloro-2,4-dinitrobenzene and of piperidine were prepared in the desired binary solvent mixture at room temperature. The reactions were run by mixing known amounts of each solution in the thermostated cells of the spectrophotometer, recording the absorbances at 400 nm. The pseudo-first-order (k_φ), and second-order (k_A), rate coefficients were obtained as described previously. In all cases, the 'infinity' value, A_∞, was experimentally determined for each run at the working temperature. Within the experimental error, this value agreed with the 'theoretical' value calculated from application of Beer's law to a solution of *N*-(2,4-dinitrophenyl)piperidine in the working binary solvent mixture.

The energies of activation were calculated from the linear regression of $\ln k_A$ versus $1/T$ by the least-squares method, and the entropies of activation were calculated by the standard equation derived from the absolute theory of reaction rates. All the kinetic runs were carried out at least in duplicate; the error in k_A is ≤2–3% for all the solvent mixtures examinated. Values of ΔH^* were accurate to ca ±0·4 kJ mol^{-1} and values of ΔS^* to ±8 J mol^{-1} K^{-1}.

$E_T(30)$ measurements. The pure solvents were mixed in an appropriate proportions by weight to give binary solvent mixtures of various compositions. 2,4-Diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate solutions were prepared just prior to use. Visible spectra of sample solutions in 10 mm cell were recorded at 15 and 40 °C by using a Perkin-Elmer Model 124 UV–VIS spectrophotometer and a Zeiss PMQ 3 UV–VIS spectrophotometer equipped with a data-acquisition system and a thermostated cell holder. Temperatures were measured in the cell and were accurate to within ±0·1 °C. The $E_T(30)$ values were determined from the longest-wavelength UV–VIS absorption band of Reichardt's betaine dye and were calculated according to the equation $E_T(30)$ [kcal mol^{-1}] $= hc\nu N = 2{\cdot}859 \times 10^{-3}\nu$ [cm^{-1}]

ACKNOWLEDGEMENTS

We are indebted to the Universidad Nacional del Litoral (UNL), República Argentina. This work received financial support from the Science and Technology Secretariat-UNL-CAI+D Program (Project 94-0858-007-054).

REFERENCES

1. C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed. Verlag Chemie, Weinhein (1988).
2. C. Reichardt, *Angew. Chem., Int. Ed. Engl.* **4**, 29 (1965).
3. K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, *Justus Liebigs Ann. Chem.* **1**, 661 (1963).
4. (a) L. G. S. Brooker, A. C. Craig, D. W. Heseltine, P. W. Jenkins and L. L. Lincoln, *J. Am. Chem. Soc.* **87**, 2443 (1965); (b) D. Walter, *J. Prakt. Chem.* **316**, 604 (1974); (c) S. Brownstein, *Can. J. Chem.* **38**, 1590 (1960); (d) E. M. Kosower, *An Introduction to Physical Organic Chemistry*, p. 293. Wiley, New York (1968); (e) J. E. Dubois and A. Bienvenue, *J. Chim. Phys.* **65**, 1259 (1968); (f) A. Allerhand and P. Schleyer, *J. Am. Chem. Soc.* **85**, 371 (1963); (g) B. R. Knauer and J. J. Napier, *J. Am. Chem. Soc.* **98**, 4395 (1976); (h) V. Gutmann, *Chemtech* 255 (1977), and references cited therein; (i) M. J. Kamlet and R.W. Taft, *J Org. Chem.* **47**, 1734 (1982), and references cited therein; (j) E. Buncel, S. Rajagopal, *J. Org. Chem.* **54**, 798 (1989).
5. (a) I. A. Koppel and V. A. Palm, *Reakts. Sposobn. Org. Soedin.* **8**, 291 (1971); *Engl. Edn.* **11**, 137 (1974); N. B. Chapman and J. Shorter (Eds), *Advances in Linear Free-Energy Relationships*. Plenum Press, London (1972);

(b) T. M. Krygowski and W. R. Fawcett, *J. Am. Chem. Soc.* **97**, 2143 (1975); (c) R. C. Dougherty, *Tetrahedron Lett.* 385 (1975); (d) F. W. Fowler, A. R. Katritzky and R. D. Rutherford, *J. Chem. Soc. B* 460 (1971); (e) C. G. Swain, *J. Org Chem.* **49**, 2005 (1984); C. G. Swain, A. L. Powell and S. Alunni, *J. Am. Chem. Soc.* **105**, 502 (1984); (f) M. J. Kamlet, J. L. Abboud and R. W. Taft, *J. Am. Chem. Soc.* **99**, 6027 (1977); R. S. Drago, M. Hirsch, D. C. Ferris and C. Chronister, *J. Chem. Soc., Perkin Trans.* 2 219 (1994).

6. (a) M. H. Abraham, *J. Phys. Org. Chem.* **6**, 660 (1993); (b) *Pure Appl. Chem.* **65**, 2503 (1993).
7. (a) J. F. Bunnett and R. J. Morath, *J. Am. Chem. Soc.* **77**, 5051 (1955); (b) **77**, 5165 (1955).
8. C. F. Bernasconi, in *MTP International Series in Organic Chemistry, Series One*, edited by H. Zollinger, Vol. I. Butterworth, London (1973).
9. (a) C. Reichardt, *Angew. Chem., Int. Ed. Engl.* **18**, 98 (1979); (b) J. N. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed. Academic Press, New York (1992).
10. (a) P. M. Mancini, L. R. Vottero, R. D. Martinez and N. S. Nudelman, *J. Chem. Soc., Perkin Trans. 2* 1133 (1984); (b) *Ac. Sudam. Qca.* **2**, 19 (1982).
11. P. M. Mancini, L. R. Vottero, R. D. Martinez and N. S. Nudelman, *J. Chem. Soc., Perkin Trans. 2* 1427 (1986).
12. R. W. Taft, in *Steric Effects in Organic Chemistry*, edited by M. S. Newman, Chapt. 13. Wiley, New York, (1956).
13. P. M. Mancini, L. R. Vottero, R. D. Martinez and N.S. Nudelman, *An. Soc. Cient. Arg.* **211**, 27 (1981).
14. (a) C. F Bernasconi and H. Zollinger, *Helv. Chim. Acta* **49**, 103 (1965); (b) *Tetrahedron Lett.* 1083 (1965); (c) F. Pietra and A. Fava, *Tetrahedron Lett.* 1535 (1963); (d) W. Greizerstein and J. Brieux, *J. Am. Chem. Soc.* **84**, 1032 (1962); (e) S. D. Ross and M. Finkelstein, *J. Am. Chem. Soc.* **85**, 2603 (1963); (f) N. Danilova and S. Shein, *Sposobnost. Org. Soedin.* **4**, 649 (1967).
15. (a) M. Rosés, F. Rived and E. Bosch, *J. Chem. Soc., Faraday Trans.* **89**, 1723 (1993); (b) E. Bosch and M. Rosés, *J. Chem. Soc., Faraday Trans.* **88**, 3541 (1992).
16. (a) Y. Marcus, *Chem. Soc. Rev.* **22**, 409 (1993); (b) *Ion Solvation.* Wiley, New York (1995)
17. P. M. Mancini, A. Terenzani, M. G. Gasparri and L. R. Vottero, *J. Phys. Org. Chem.* **8**, 617 (1995).
18. M. J. Kamlet, R. Doherty, R. W. Taft and M. H. Abraham, *J. Am. Chem. Soc.* **105**, 6741 (1983).
19. R. M. C. Goncalves, A. M. N. Simoes, L. M. P. Albuquerque, M. Rosés and E. Bosch, *J. Chem. Res. (M)* 1380 (1993); *(S)* 214 (1993).
20. J. F. Bunnett and R. H. Garst, *J. Am. Chem. Soc.* **87**, 3879 (1965).
21. C. F. Bernasconi, C. L. Gerigher and R. H. Rossi, *J. Am. Chem. Soc.* **99**, 4090 (1977).
22. (a) J. E. Sinsheimer and A. M. Keuhnelian, *Anal. Chem.* **16**, 89 (1974); (b) S. D. Prahan and H. B. Mathews, *Proc. Indian Acad. Sci., Sect. A* **87**, 23 (1978); (c) M. Kern, D. Servals, L. Abello and G. Pannetier, *Bull. Soc. Chim. Fr.* 2763 (1969).
23. Reviews on solvent polarity scales: (a) C. Reichardt, in *Solvent Scales and Chemical Reactivity. Organic Liquids–Structure, Dynamics and Chemical Properties*, edited by A. D. Buckingham, E. Lippert and E. Bratos, pp. 269–291. Wiley, New York (1978); (b) J. L. Abboud, M. J. Kamlet and R. W. Taft, *Prog. Phys. Org. Chem.* **13**, 485 (1981); (c) T. W. Bentley and G. Llewellyn, *Prog. Phys. Org Chem.* **17**, 12 (1990); (d) E. Buncel and S. Rajagopal, *Acc. Chem. Res.* **23**, 226 (1990).
24. P. R. Wells, *Linear Free-Energy Relationships.* Academic Press, London (1968).
25. N. B. Chapman and J. Shorter, *Advances in Linear Free-Energy Relationships.* Plenum Press, London (1972).
26. J. Shorter, *Correlation Analysis in Organic Chemistry. An Introduction to Linear Free-Energy Relationships.* Clarendon Press, Oxford (1973).
27. C. Reichardt, *Chem. Rev.* **94**, 2319 (1994).
28. (a) Y. Migron and Y. Marcus, *J. Chem. Soc., Faraday Trans.* **87**, 1339 (1991); (b) Y. Marcus, *J. Chem. Soc., Perkin Trans. 2* 1015 (1994).
29. (a) E. Bosch, C. Rafols and M. Rosés, *Anal. Chem.* **62**, 102 (1990); (b) E. Bosch, F. Rive and M. Rosés, *J. Phys. Org. Chem.* **7**, 696 (1994).
30. C. Reichardt, S. Asharin-Fard, A. Blum, M. Eschner, A. M. Mehranpour, P. Milart, T. Niem, G. Schafer and M. Wilk, *Pure Appl. Chem.* **65**, 2593 (1993).
31. S. Balakrishnan and A. J. Easteal, *Aust. J. Chem.* **34**, 933 (1981).
32. Y. Marcus and Y. Migron, *J. Phys. Chem.* **95**, 400 (1991).
33. (a) R. I. Zalenski, Y. Adamczewska and C. Reichardt, *J. Chem. Res. (S)* 280 (1990); (b) C. Reichardt and E. Harbusch-Görnert, *Liebigs Ann. Chem.* 721 (1983); (c) W. Linert and R. F. Jameson, *J. Chem. Soc., Perkin Trans. 2* 1415 (1993).
34. A. I. Vogel, *Practical Organic Chemistry*, 5th ed. Longman, London (1991).