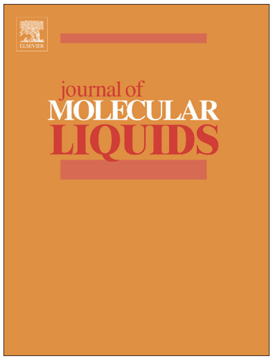

Binary mixtures of dimethyl sulfoxide with methanol, ethylene glycol, and glycerol as solvent: Solvatochromism and chemical kinetics study

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Binary mixtures of dimethyl sulfoxide with methanol, ethylene glycol, and glycerol as solvent: Solvatochromism and chemical kinetics study

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Abstract

The understanding of solvent effects on chemical reaction requires precise knowledge of solute-solvent interactions. Since solute-solvent interactions are much more complex in mixed solvents, the study of chemical kinetics can be valuable because of the possibility of preferential solvation. In this work, binary mixture of methanol-DMSO, ethylene glycol-DMSO, and glycerol-DMSO were selected as solvent systems to determine solvatochromic polarity parameters and investigate the solute-solvent and solvent-solvent interactions. Results showed that the variation of parameters respect to solvent composition in these mixtures were compatible with those of in deep eutectic solvents-DMSO mixtures including ethylene glycol and glycerol. Aromatic nucleophilic substitution reaction of 1-fluoro-2,4-dinitrobenzene with piperidine was also investigated in the mentioned mixtures. Kinetic data showed that the reaction strongly follows the based-catalyzed mechanism in DMSO rich region. The partial catalytic and non-catalytic rate coefficients demonstrated reasonable correlations with solvatochromic parameters.

Keywords: Aromatic nucleophilic substitution; 1-Fluoro-2,4-dinitrobenzene; Solvatochromic parameters; Preferential solvation; Solvent effect.

1. Introduction

Solvent can have an effect on solubility, selectivity, and reaction rates and choosing the suitable solvent allows for thermodynamic and kinetic control over a chemical reaction [1–4]. The effect of solvent on chemical reactivity has previously been explained on the basis of the dielectric constant, viscosity, dipole moment, internal pressure and so on. However it has been proved that the solvent effects are related to the nature of solute-solvent interactions. These interactions can be influenced by the attributes of solvent molecules. The ionic or non-ionic nature of the molecules and the existence of functional groups determine the type and strength of solute-solvent interactions [5]. Therefore, solvent effects are commonly interpreted as resulting from changes in media polarity, a general term that is related to the overall solvating capability of the solvent [6]. Due to the complexity of the solvation phenomena and solute-solvent interactions, there are no reliable and exact methods for a quantitative description and prediction of these interactions. Empirical parameters of solvent polarity are of great value in this respect and can be derived with the aid of the principle of linear free energy relationships [7–11]. We have continuously studied the solvatochromism of solvatochromic indicators and also the kinetics of chemical reactions in pure and binary solvent mixture consisting of ionic liquids (ILs) or deep eutectic solvents (DESs) [12–15].

Solute-solvent interactions are much more complex in mixed solvents than those of in pure solvents because of the possibility of preferential solvation and solvent-solvent interactions [16–20]. Our research group has tried to investigate these interactions in binary mixtures including new solvents such as ILs or DESs. In recent contribution [21], we have found that DESs have a dramatic effect on the rate of aromatic nucleophilic substitution (S_NAr) reaction. A similar trend has been observed in the variation of rate coefficient when 1-butyl-3-methyl imidazolium tetrafluoroborate as an ILs was added to molecular solvents. [22].

In this work, we have determined the solvatochromic parameters of binary mixture of ethylene glycol and glycerol, as basic component of two DESs, with dimethyl sulfoxide (DMSO). Binary mixtures of methanol-DMSO have been also studied to compare the effect of methanol on solvatochromic parameters with that of polyols. In order to investigate the influence of solvent effects on the chemical reaction rate, the chemical kinetics of a selected S_NAr reaction were studied in the binary solvent mixture of methanol, ethylene glycol, and glycerol with DMSO.

2. Experimental section

2.1. Materials

Methanol (≥99.8%), ethylene glycol (≥99.8%), glycerol (≥99.5%, spectrophotometric grade), and spectroscopic grade of DMSO were purchased from Merck. All solvents were dried by 3Å molecular sieve. The water content of the dried materials was determined by coulometric Karl Fisher titration yielding < 1000 ppm residual water. 4-Nitroanisol and 4-Nitroaniline (> 99%) were recrystallized from water/ethanol and water/acetone, respectively, Reichardt's betaine dye (>90%) was obtained from Sigma-Aldrich and was used without further purification.

2.2. Spectrophotometric measurements

In order to determine the maximum absorption of 4-nitroanisole, 4-nitroaniline, and Reichardt's betaine dye, aliquot of their primary solutions were transferred into a 1 cm quartz cuvette. The binary mixtures of solvents over the entire range of mole fractions were gravimetrically prepared (±0.1mg uncertainty in mixture composition). Each binary mixture was transferred into the quartz cell and the solution was vigorously stirred, so that a homogeneous solution was prepared. UV-vis absorption spectra of the solutions were recorded in the suitable range of wavelength, using a GBC UV-vis cintra 101 spectrophotometer at 25˚C.

2.3. Kinetic measurements

The kinetic of the reaction between 1-flouro-2, 4-dinitrobenzene (FDNB) and piperidine (Pip) was spectrophotometrically studied in the mixtures of DMSO with methanol, ethylene glycol, and glycerol at 25˚C. Prior to kinetic investigations, the product of the reaction was synthesized by adding of Pip to FDNB directly and then the recrystallizing of the produced precipitate from hot ethanol. The stability of product was tested in all solvents for 24h. Solvent mixtures were closely prepared as described in previous section. After transferring the aliquot of primary solutions of the reactants, the variation of solution absorption was recorded at a wavelength around 360-370 nm depending on the solvent composition. The concentrations of FDNB and Pip were chosen in significant difference to study the reaction under pseudo-first-order conditions. The rate coefficients of the reaction were calculated according to the procedure reported in elsewhere [23,24].

3. Results and discussion

3.1. Solvatochromic parameters in binary solvent mixtures

The solvatochromic parameters of pure methanol, ethylene glycol, glycerol, and their mixtures with DMSO including hydrogen bond donor ability, α, hydrogen bond acceptor ability, β, dipolarity/polarizability, π^*, and normalized polarity, E_T^N, of media over the entire composition range have been determined based on the procedure reported elsewhere [12]. Eqs 1–4 show the related equations used to determine the solvatochromic parameters:

$$E_T(30)/\mathrm{kcal.\,mol^{-1}} = 2.8592\,\vartheta_B \qquad (1)$$

$$E_T^N = \frac{E_T(\mathrm{solvent}) - E_T(\mathrm{TMS})}{E_T(\mathrm{water}) - E_T(\mathrm{TMS})} \qquad (2)$$

$$\pi^* = 0.427(34.12 - \vartheta_{ANS}) \qquad (3)$$

$$\beta = \frac{31.10 - 3.14\pi^{*} - \vartheta_{ANI}}{2.79} \qquad (4)$$

$$\alpha = 0.186(10.91 - \vartheta_{B}) - 0.72\pi^{*} \qquad (5)$$

where ϑ_B, ϑ_{ANS} , and ϑ_{ANI} are the wavenumbers of maximum absorbance Reichardt’s betaine dye, 4-nitroanisole, and 4-nitroaniline, respectively, in kK. $E_T(30)$ is empirical polarity and refers to charge transfer energy of Reichardt’s betaine dye in solvent that its values have been reported as normalized parameters (E_T^N) in this contribution. TMS denotes tetramethyl silane. Determined solvatochromic parameters based on recent equation were reported in Table 1. Fig. S1 of the supplementary materials shows that the trends of present data are in good agreement with solvatochromic parameters of ethaline-DMSO and glyceline-DMSO mixtures recently published by our research group [14]. Ethaline and glyceline, as two usual DESs, are consisting of ethylene glycol and glycerol, respectively. With relative deviations generally <12%, except for the β parameter of glycerol, solvatochromic parameters of pure ethylene glycol and glycerol demonstrate a relative agreement with the solvatochromic parameter value of pure DESs. On the other hand, the similar trend of data variation respect to mole fraction, with relative deviation between 5.2-41.5% (exhibited in Fig. S1), confirms that ethylene glycol and glycerol are dominant components which determine the polarity of DESs. It is worth mentioning that the determining factor of media polarity is polyol moiety and DESs.

Deviation from ideal behaviour produces an excess values for solvatochromic parameters which can be concluded the probes are not equally solvated by the two components of the binary solvent mixture and a preferential solvation of the probe is occurred. These conditions arise when the composition of bulk solvated differs from the solvation microsphere.

3.2. Preferential solvation model

As it can be found in various reports, preferential solvation model is based on a simple exchange of two solvents in microsphere solvation of an indicator (solute) according to the following equations:

$$\text{I (S1)2 + 2S2} \rightleftharpoons \text{I (S2)2 + 2S1} \qquad (6)$$

$$\text{I (S1)2 + S2} \rightleftharpoons \text{I (S12)2 + S1} \qquad (7)$$

where I stands for the solute, S1 and S2 for the pure solvents, and S12 for the solvent formed by the interaction of solvents 1 and 2. I(S1), I(S2) and I(S12) represent the solute solvated by the S1, S2 and S12 species. Eq. (6) reflects the total exchange of solvent 1 by solvent 2 in the solvation sphere of the solute, and Eq. (7) corresponds to the exchange by the double-structure solvents. The constants of two processes are defined by the preferential solvation parameters $f_{2/1}$ and $f_{12/1}$ according to the Eqs (8) and (9) [25–27]:

$$f_{2/1} = \frac{x_2^s/x_1^s}{(x_2^0/x_1^0)^2} \qquad (8)$$

$$f_{12/1} = \frac{x_{12}^s/x_1^s}{x_2^0/x_1^0} \qquad (9)$$

where x_1^s, x_2^s, and x_{12}^s are the mole fractions of the solvent 1, 2, and composite solvent, respectively, in solvation microsphere. x_1^0 and x_2^0 represents the bulk mole fractions of solvent 1 and 2, respectively. According to this model, the physio-chemical properties (Y) in the solvent mixtures are calculated as an average of these properties in pure and composite solvents (Y_1, Y_2, and Y_{12}) as follows:

$$Y = \frac{Y_1(1 - x_2^0) + Y_2 f_{2/1}(x_2^0) + Y_2 f_{12/1}(1 - x_2^0)x_2^0}{(1 - x_2^0)^2 + f_{2/1}(x_2^0) + f_{12/1}(1 - x_2^0)x_2^0} \qquad (10)$$

In this study, Y refers to the wavenumber of solvatochromic indicators in solution. In the continuing of this contribution, x_2^0 has been demonstrated with x_{CoS} that refers to the mole fraction of methanol, ethylene glycol, and glycerol in binary solvent mixtures. Solvent effects on the solvation of indicator can be observed with the hypso- or batho-chromic band shift of the absorbance spectra. Deviations from the ideal trends of wave numbers are related to difference between the solvation microsphere and bulk compositions.

A pronounced trend with a regular sequence is observed for the absorbance wave numbers of 4-nitroanisole, that is, methanol-DMSO mixtures show fast variation while glycerol-DMSO mixtures demonstrate a negligible variation (Fig. 1a). On the other side, the wave numbers of 4-Nitroaniline show a similar trend in all mixtures (Fig. 1b). It is clear that the Reichardt's betaine dye presents an increasing trend with a positive deviation from ideality, minimum deviation in methanol-DMSO and maximum deviation in glycerol-DMSO mixtures (Fig. 1c)

The measured wave numbers of solvatochromic probes have been fitted to the proposed Eq. (10) and the calculated parameters are given in Table 2. In all probes and mixtures, data shows that $f_{2/1}$ values are little more or less than unit except for betaine dye in ethylene glycol-DMSO and glycerol-DMSO. It means that this indicator is preferentially solvated by ethylene glycol or glycerol. On the other hand, high $f_{12/1}$ values in the majority of data demonstrate that also the indicators (especially betaine dye) can be preferentially solvated by the composite solvents compared to pure DMSO. A comparison of the preferential solvation of betaine dye in this work with previous contribution [21] indicates that this probe is preferentially solvated by the polyol moiety of DESs.

3.3. Kinetic results

In order to investigate the influence of solvent polarity parameters and compare the solvent effects in ethylene glycol-DMSO and glycerol-DMSO with DESs-DMSO media, the S_NAr reaction between FDNB and Pip was studied in methanol-DMSO, ethylene glycol-DMSO, and glycerol-DMSO mixtures. The mentioned media were selected regarding to similar study recently published [21] in order to determine the influence of molecule solvent or salt moiety in DESs as a dominant component which affects on chemical kinetics of the reaction.

The suggested reaction mechanism of FDNB with Pip has been shown in Scheme 1 with apparent rate coefficient according to Eq. (11) [24]:

$$k_A = \frac{k_1(k_2 + k_3[B])}{k_{-1} + k_2 + k_3[B]} \qquad (11)$$

where k_A is the apparent second-order rate coefficient and B is Pip as both nucleophile and base catalyst. It has been proved that if the decomposition of the intermediate to products is slow, Eq. (11) will be rearranged to Eq. (12):

$$k_A = \frac{k_1 k_2}{k_{-1}} + \frac{k_1 k_3}{k_{-1}}[B] \qquad (12)$$

It is clear that the apparent rate coefficient is related to Pip concentration. On the other word, the reaction follows a base-catalyzed mechanism. It was confirmed that base-catalyzed or non-catalyzed mechanism of the reaction is related to not only the nature of the reactants but also the solvent properties [22–24].

In order to determine the mechanism of the reaction, the influence of Pip concentration, as a base, on the reaction rate was studied over the entire range of DMSO mole fractions in methanol-DMSO, ethylene glycol-DMSO, and glycerol-DMSO mixtures. The obtained second order rate coefficients of the reaction are summarized in Table 3 as a function of Pip concentration in all solvent mixtures. Data shows that the reaction follows the base-catalyzed mechanism in the most of solvent mixtures.

Fig. S2 shows the influence of solvent composition on the reaction rate. Also, it demonstrates different kinetics response depending on the solvent composition. The dependence of k_A values on Pip concentration in the DMSO region is higher than those of methanol, ethylene glycol, or glycerol regions. In all mixtures, the statistical parameters reveal a satisfactory linear dependence of the rate coefficient on the change in Pip concentration (Table 4). On the other hand, the observable changes are clear in the trends of rate coefficient when the solvent composition changes. The k_A values decrease smoothly with increasing mole fraction of methanol in methanol-DMSO mixtures while it decreases sharply with adding the ethylene glycol and glycerol as a co-solvent to DMSO. Fig. S3 demonstrates the similarity trend between data in this contribution with previous report [21] reported in ethaline-DMSO and glyceline-DMSO mixtures. It confirms that ethylene glycol and glycerol in ethaline and glyeline, respectively, are effective moieties on the reaction mechanism. Data in Table 4 shows that reaction has the highest value of k_1k_3/k_{-1} in pure DMSO compared with in all solvent mixtures. Like ethaline-DMSO and glyceline-DMSO, which exhibit and exponential increasing of k_1k_3/k_{-1} with respect to DMSO mole fraction [21], a sharp enhancement of k_1k_3/k_{-1} values is clear when the mole fraction of solvent mixture increases respect to DMSO in all mixtures. The results in the pure solvents indicate that the reaction is clearly base-catalyzed in DMSO and it is less influence by catalysis in methanol, ethylene glycol, and glycerol (Table 3). In all mixtures, the k_2/k_3 values reveal that the reaction is base-catalyzed over the whole range of mixed solvent compositions. On the other word, the reaction is susceptible to be base-catalyzed when it is performed in pure DMSO or DMSO-rich mixtures. On the other hand, it is partially base-catalyzed or non-catalyzed in pure alcohol and alcohol-rich region.

These results are compatible with the similar influences of hydrogen bond donor (HBD) or non-HBD solvents on the base catalysis in S_NAr reactions [22,24,28,29]. The performed reaction in solvents with HBD ability (such as methanol) exhibits non-catalyzed mechanism while it follows base-catalyzed mechanism in some hydrogen bond acceptor (HBA) solvents.

3.4. Solvent effects on partial rate coefficients

As it was mentioned above, solvent composition controls the reaction mechanism and it will be truly in relation with solvent properties. In order to find relationship between the base-catalyzed mechanism and solvent effects, we analyzed the influence of the microscopic solvent properties on the base catalysis rate coefficients k_1k_3/k_{-1} and k_1k_2/k_{-1}, in which the former is related to the catalyzed step and the later refers to the non-catalyzed step of the reaction. The variation of these partial rate coefficients were investigated as a function of solvent composition and also solvatochromic parameters (E_T^N, α, β, and π^*). The results have been exhibited in Figs. 2-4.

The plot k_1k_3/k_{-1} *vs* x_{Cos} (co-solvent is methanol, ethylene glycol, or glycerol) shows that the partial rate coefficient k_1k_3/k_{-1} non-linearly decreases with mole fraction of co-solvent (Fig. 2a-4a).

Inset curves of Figs. 2-4 demonstrate a similar pattern for the variation of k_1k_2/k_{-1} *vs* x_{Cos} in all mixtures. It is clear that there is an obvious difference among the changes in rate coefficients so that k_1k_3/k_{-1} and k_1k_2/k_{-1} decrease smoothly from pure DMSO to pure methanol while they diminish sharply from pure DMSO (in while the base catalysis is effective) to pure ethylene glycol or glycerol (in which the non-catalyzed mechanism is possible). These results refer to the tendency of reaction to follow the base-catalyzed mechanism over the entire range of mole fractions in methanol-DMSO mixtures (Fig. 2a). Similar tendencies are observed in ethylene glycol-DMSO and glycerol-DMSO mixtures (Figs. 3a and 4a).

In order to investigate and evaluate the solvent effects on the partial rate coefficients, the relationship between k_1k_3/k_{-1} or k_1k_2/k_{-1} and solvatochromic parameters was studied (Figs. 2-4). The plots show increases in both k_1k_3/k_{-1} and k_1k_2/k_{-1} with increments in the dipolarity/polarizability while both of them decrease with increasing the HBD ability of the media in methanol-DMSO and ethylene glycol-DMSO. It is worth mentioning that the dipolarity/polarizability and HBD ability of the media have opposite effects on the reaction rate. Since the intermediate of the reaction has zwitterionic character and the activated complex of the reaction has higher polarity than reactants, the reaction rate increases with the dipolarity/polarizability. On the other hand, hydrogen bond donor solvents interact with nucleophile through the hydrogen-bonding interactions. Therefore, the nucleophile is stabilized and the reaction rate decreases when HBD ability of the media increases. The decreasing trend of k_A with mole fraction of methanol and ethylene glycol in methanol-DMSO and ethylene glycol-DMSO, respectively, confirms that the HBD ability of media which affects on the reaction rate is the most effective factor as a rate coefficient controller. Although Fig. 4 shows the different pattern of partial rate coefficients *vs* dipolarity/polarizability, correlation between reaction coefficients and HBD ability of the media is the same. Consequently, the influence of the HBD ability on the reaction rate can be interpreted in the same way.

On the other hand, these plots show that k_1k_3/k_{-1} and k_1k_2/k_{-1} enhance with increasing HBA ability of the media. It means that high HBA solvents are suitable media for base catalysis condition in the reaction.

The correlation of partial rate coefficients with empirical polarity (E_T^N) is present in Figs. S4-S6 in which decreases in partial rate coefficients are observed with increment in E_T^N. since there is a dual parameter regression for E_T^N as a function of dipolarity/polarizability and HBD [9], it is expectable that a particular pattern is observed like dipolar/polarizability or HBD pattern. It shows that the reaction is performed in the solvent media with low polarity (not low polarizability) with the highest partial base catalyzed and non-catalyzed rate coefficients. The adding of co-solvent with different characterization decreases sharply the rate coefficients.

4. Conclusions

The comparison of solvatochromic parameters determined in binary mixtures of methanol-DMSO, ethylene glycol-DMSO, and glycerol-DMSO with those of in binary mixtures of ethaline and glyceline with DMSO shows that it can be concluded similar trend of parameters with solvent composition in the most of them. On the other hand, it confirms that the ethylene glycol and glycerol in their corresponding DESs, ethaline and glyceline, respectively, are the most effective moieties of DESs which determine the physico-chemical properties of DESs.

The S_NAr reaction of 1-fluoro-2,4-dinitrobenzene with piperidine performed in the mixtures of methanol, ethylene glycol, and glycerol with DMSO showed a similar pattern with DESs-DMSO mixtures. Empirical polarity and HBD ability of the media have parallel and positive effects on the both apparent and partial rate coefficients. On the other hand, the reaction follows the catalyzed mechanism by piperidine in DMSO and DMSO-rich mixtures.

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Table 1. Solvatochromic parameters for binary solvent mixtures of methanol, ethylene glycol, and glycerol with DMSO at 25˚C (x_{CoS} refers to the mole fraction of methanol, ethylene glycol, or glycerol).

DMSO												
	Methanol				**Ethylene glycol**				**Glycerol**			
x_{CoS}	α	β	π^*	E_T^N	α	β	π^*	E_T^N	α	β	π^*	E_T^N
0	0.12	0.91	1.12	0.45	0.12	0.91	1.12	0.45	0.12	0.91	1.12	0.45
0.1	0.31	0.95	1.03	0.52	0.36	0.90	1.09	0.56	0.42	0.86	1.12	0.59
0.2	0.43	0.96	1.00	0.56	0.49	0.91	1.06	0.61	0.51	0.83	1.14	0.64
0.3	0.52	0.98	0.97	0.60	0.62	0.90	1.03	0.66	0.58	0.74	1.15	0.68
0.4	0.62	0.95	0.95	0.64	0.66	0.87	1.00	0.67	0.60	0.67	1.17	0.70
0.5	0.71	0.92	0.92	0.67	0.73	0.83	1.00	0.70	0.66	0.61	1.17	0.73
0.6	0.78	0.91	0.88	0.69	0.79	0.81	0.99	0.73	0.68	0.57	1.15	0.73
0.7	0.87	0.86	0.83	0.71	0.86	0.80	0.96	0.75	0.74	0.53	1.14	0.75
0.8	0.94	0.82	0.79	0.73	0.90	0.79	0.93	0.76	0.81	0.47	1.11	0.78
0.9	0.99	0.81	0.77	0.75	0.94	0.71	0.91	0.77	0.82	0.38	1.15	0.79
1	1.04	0.78	0.74	0.76	0.95	0.61	0.95	0.79	0.86	0.36	1.12	0.81

Table 2. Parameters and standard deviation obtained by using of the preferential solvation model based on Eq. (10).

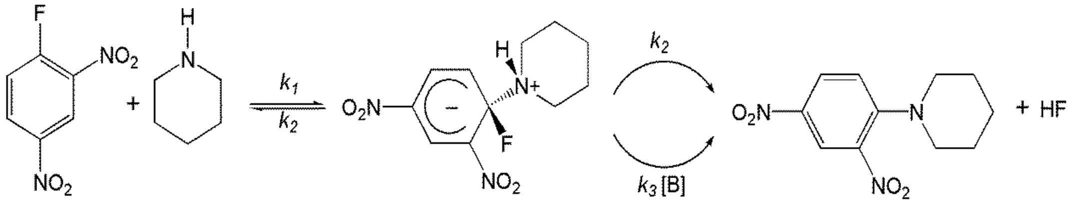
Indicator	Solvents	Y_1	Y_2	Y_{12}	$f_{2/1}$	$f_{12/1}$	N	r^2	σ
4-Nitroanisole	**DMSO/methanol**	31.54	32.39	32.01	**1.10**	2.49	11	0.980	0.002
	DMSO/ethylene glycol	31.51	31.94	31.90	1.00	1.71	11	0.951	0.001
	DMSO/glycerol	31.50	31.50	31.27	1.00	1.10	11	0.959	0.002
4-Nitroaniline	**DMSO/methanol**	25.09	26.61	25.53	0.72	1.00	11	0.992	0.002
	DMSO/ethylene glycol	25.06	26.43	25.74	0.42	1.61	11	0.991	0.002
	DMSO/glycerol	25.06	26.57	25.92	0.55	1.09	11	0.994	0.002
Betaine dye	**DMSO/methanol**	15.91	19.36	18.64	1.00	2.28	11	0.993	0.009
	DMSO/ethylene glycol	15.88	19.68	18.81	2.53	5.02	11	0.997	0.005
	DMSO/glycerol	15.90	19.91	18.82	2.84	8.04	11	0.988	0.007

Table 3. Second-order rate coefficients, $\boldsymbol{k_A}$ / Lmol^{-1} s^{-1}, for the reaction between 1-fluoro-2,4-dinitrobenzene (2×10^{-5} mol L^{-1}) and piperidine in binary solvent mixtures, measured at 25˚C.

		[pip] / mol L^{-1}					
solvent	x_{CoS}	**0.0002**	**0.0004**	**0.001**	**0.0014**	**0.002**	**0.0024**
DMSO	0.0	400.0	460.0	520.0	610.0	-	-
methanol		3	5	6	7	7.5	8.3
ethylene glycol		-	8.1	9.4	10.7	12	14.75
glycerol		-	2	3	5	5	6.13
DMSO+methanol	0.1	350	370	426	485	540	586
DMSO+ethylene glycol		-	78.25	150.1	195.8	232.6	270.2
DMSO+glycerol		-	71.5	90	100	116.5	141
DMSO+methanol	0.2	252	290	315	343	365	412
DMSO+ethylene glycol		-	42.04	56.7	67.8	95.7	105
DMSO+glycerol		-	11.7	16.7	20.1	23.7	30.2
DMSO+methanol	0.3	141	162	194	242	255	291
DMSO+ethylene glycol		-	18.7	20	22.2	33.6	34.4
DMSO+glycerol		-	2	2.6	4.1	5.2	7
DMSO+methanol	0.4	102	120	149	173	186	214
DMSO+ethylene glycol		-	6.0	7.1	8.4	12	13.7
DMSO+glycerol		-	1.3	2.3	3.7	4.2	5.9
DMSO+methanol	0.5	53.3	75	111	128	150	170
DMSO+ethylene glycol		-	2	3.5	4.1	5	7.1
DMSO+glycerol		-	1.5	2.1	3.2	3.8	5
DMSO+methanol	0.6	38	54	60	82	92	104
DMSO+ethylene glycol		-	1.3	2.7	3	4.3	6.8
DMSO+glycerol		-	1.2	2	2.8	3.3	4.1
DMSO+methanol	0.7	25	32	42	47	55	62
DMSO+ethylene glycol		-	1	2.5	2.9	4.2	6
DMSO+glycerol		-	1	1.9	2.3	3.2	4.3
DMSO+methanol	0.8	12	13	24	30	37	40
DMSO+ethylene glycol		-	0.6	1.5	2	3.1	4
DMSO+glycerol		-	1.4	2.4	3.1	3.5	4.6
DMSO+methanol	0.9	7	10	12	15	17.5	19
DMSO+ethylene glycol		-	2	5.5	8.1	10.8	14.1
DMSO+glycerol		-	1.8	2.8	4.2	4.9	5.9

Table 4. Partial rate coefficients for the reaction of piperidine with 1-flouro-2,4-dinitroflourobenzene in binary mixtures.

solvent	x_{CoS}	$10^{-4}\ k_1k_3/k_{-1}$ ($\mathrm{Lmol^{-1}s^{-1}}$)	k_1k_2/k_{-1} ($\mathrm{Lmol^{-1}s^{-1}}$)	$10^4k_2/k_3$	r^2	n
DMSO	0.0	15.99	377.6	23.61	0.966	4
methanol		0.21	3.6	17.14	0.953	5
ethylene glycol		0.31	6.4	20.6	0.949	5
glycerol		0.2	1.31	6.55	0.912	5
DMSO+methanol	0.1	10.78	326.5	30.29	0.997	5
DMSO+ethylene glycol		9.33	51.0	5.5	0.983	5
DMSO+glycerol		3.29	56.43	17.15	0.973	5
DMSO+methanol	0.2	6.35	251.3	39.57	0.965	5
DMSO+ethylene glycol		3.30	25.9	7.8	0.983	5
DMSO+glycerol		0.87	7.9	9.08	0.976	5
DMSO+methanol	0.3	6.57	133.1	20.26	0.974	5
DMSO+ethylene glycol		0.92	12.0	13	0.936	5
DMSO+glycerol		0.25	0.6	2.4	0.955	5
DMSO+methanol	0.4	4.77	98.5	20.65	0.980	5
DMSO+ethylene glycol		0.40	3.6	9	0.956	5
DMSO+glycerol		0.22	0.32	1.45	0.960	5
DMSO+methanol	0.5	5.04	52.4	10.40	0.979	5
DMSO+ethylene glycol		0.23	1	4.3	0.947	5
DMSO+glycerol		0.17	0.65	3.82	0.967	5
DMSO+methanol	0.6	2.83	36.8	13.0	0.63	5
DMSO+ethylene glycol		0.25	0.02	0.08	0.912	5
DMSO+glycerol		0.14	0.65	4.64	0.987	5
DMSO+methanol	0.7	1.57	24.5	15.61	0.985	5
DMSO+ethylene glycol		0.23	0.03	0.1	0.971	5
DMSO+glycerol		0.16	0.27	1.69	0.976	5
DMSO+methanol	0.8	1.35	9.4	6.96	0.984	5
DMSO+ethylene glycol		0.16	0.07	4	0.979	5
DMSO+glycerol		0.15	0.86	5.73	0.970	5
DMSO+methanol	0.9	0.52	7	13.46	0.974	5
DMSO+ethylene glycol		0.55	0.02	0.4	0.996	5
DMSO+glycerol		0.2	0.98	4.9	0.981	5



Scheme 1. The reaction mechanism of 1-fluoro-2,4-dinitrobenzene and piperidine

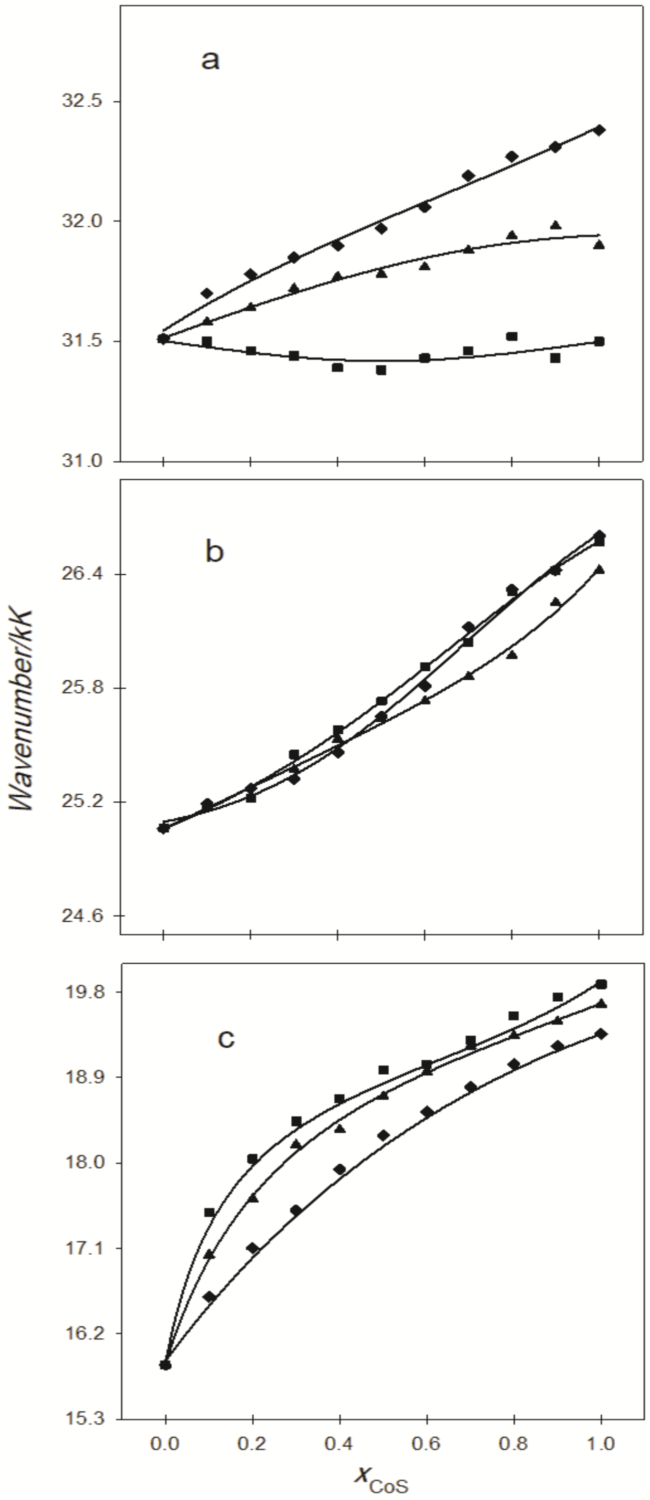


Fig. 1. The maximum absorption of wavenumber of 4-Nitroanisol (a), 4-Nitroaniline (b), and Reichardt's dye (c) for binary solvent mixtures of DMSO with methanol (♦), ethylene glycol (▲), and glycerol (■). Lines have been calculated by Eq. (10) from the parameter of Table 2.

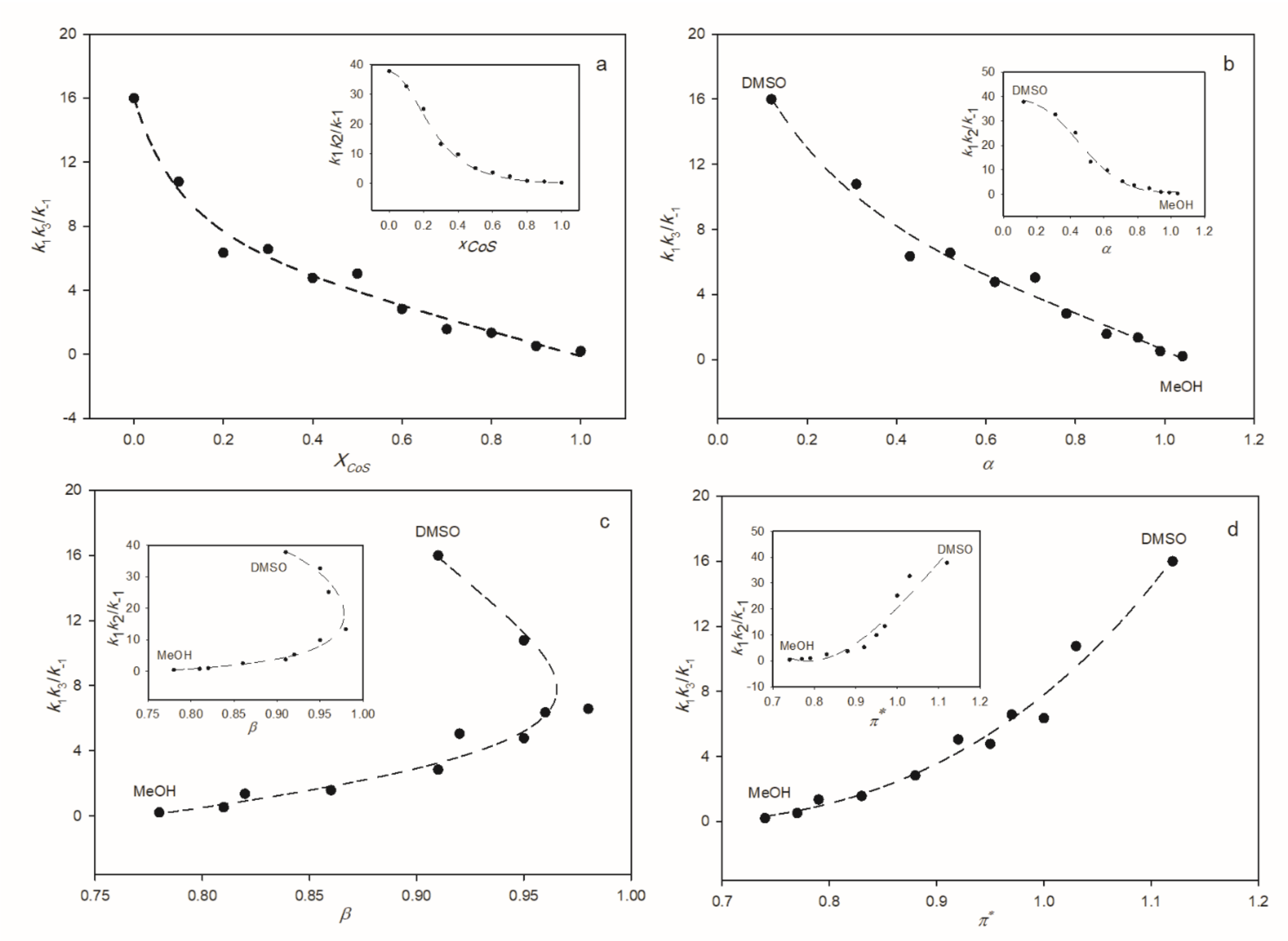


Fig. 2. Plots k_1k_3/k_{-1} and k_1k_2/k_{-1} (inset curves) *vs* x_{CoS}, α, β, and π^* for the reaction performed in DMSO-methanol mixtures.

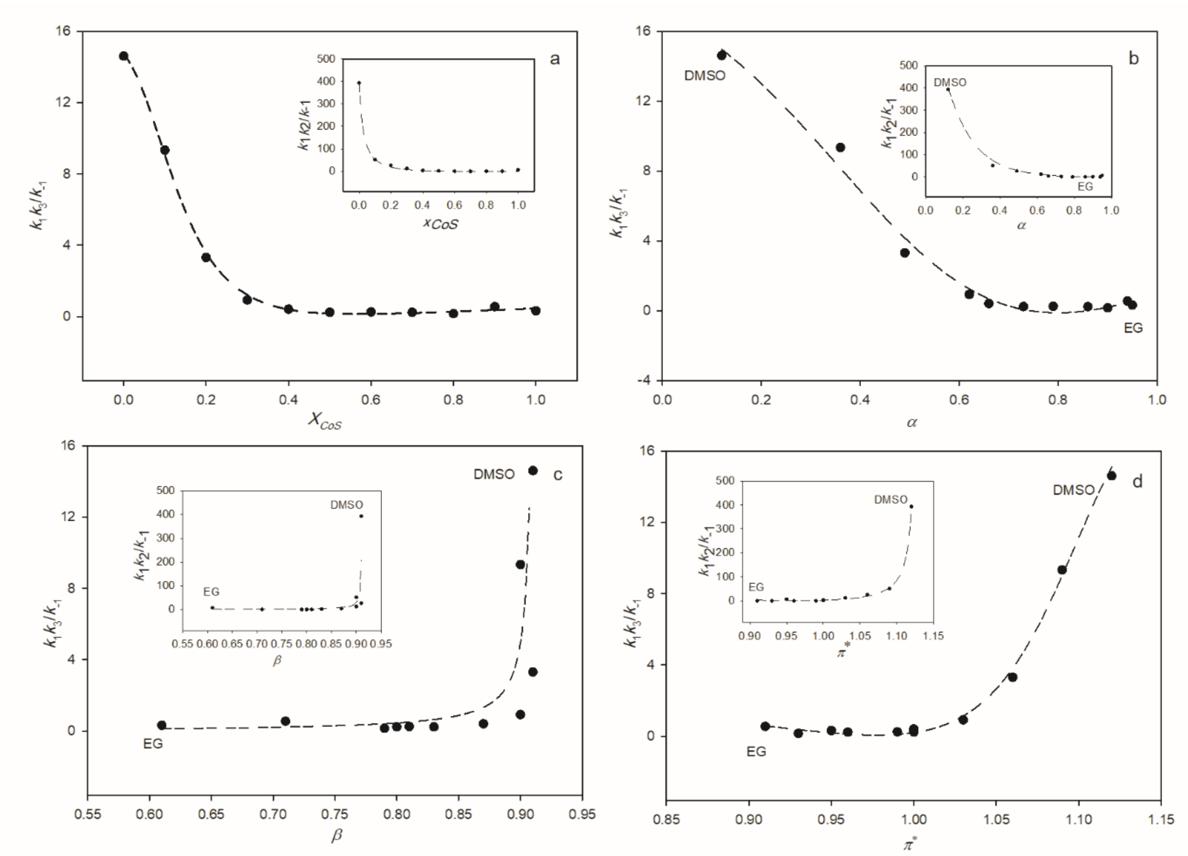


Fig. 3. Plots k_1k_3/k_{-1} and k_1k_2/k_{-1} (inset curves) *vs* x_{CoS}, α, β, and π^* for the reaction performed in DMSO-ethylene glycol mixtures.

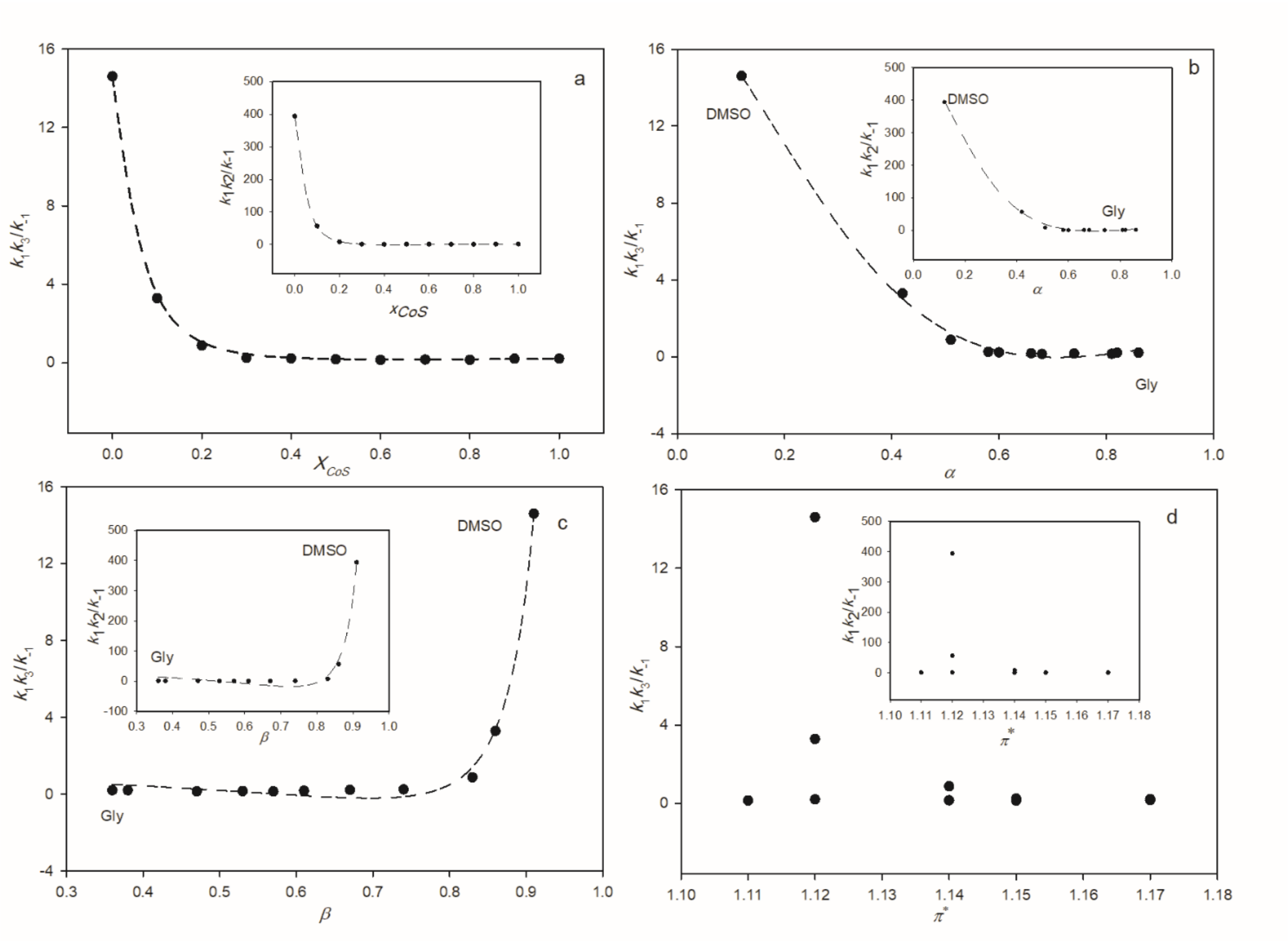


Fig. 4. Plots k_1k_3/k_{-1} and k_1k_2/k_{-1} (inset curves) *vs* x_{CoS}, α, β, and π^* for the reaction performed in DMSO-glycerol mixtures.

Highlights

- Polarity of methanol, ethylene glycol, and glycerol-DMSO mixtures was studied.
- Non-ideal trends in parameters were investigated by preferential solvation model.
- The reaction of 1-fluoro-2,4-dinitrobenzene and piperidine was studied in mixtures.
- The results were compared with data in deep eutectic solvents- DMSO mixtures.