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Solvent Effect on Reaction Rates: Reaction Between Sodium Ethoxide and Methyl Iodide in Ethanol + Cyclohexane Solvent Systems

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The kinetics of the reaction between sodium ethoxide and methyl iodide has been studied at 25°C in various cyclohexane–ethanol solvent mixtures with a cyclohexane content of 10 to 50% per volume. The determination of the rate constants at t = 0 *were carried out by a new iterative method proposed in this investigation. The obtained results show that the reaction rate decreases with the increasing cyclohexane content. This behavior can be attributed to various solute–solvent interactions of electrostatic nature. On the other hand, the variation of ion and ion pairs rate constants with solvent composition permits the various solvation effects to be taken into account.*

KEY WORDS: Solvent effect; S_N2 reaction; reactivity of ions; reactivity of ion pairs; sodium ethoxide; methyl iodide; cyclohexane–ethanol solvent mixtures.

1. INTRODUCTION

This paper is a part of our research on the kinetics of S_N2 reactions between ions and dipolar molecules in solvents where the ionic reactant associates to form ion-pairs.(1–6) At the kinetic level, these reactions are expressed by the Acree relation

$$k_g = k_p + (k_i - k_p)\alpha \tag{1}$$

where k_g is the observed rate constant, k_i and k_p the rate constants for free ions and ion-pairs as reactants and α the degree of dissociation of the ion-

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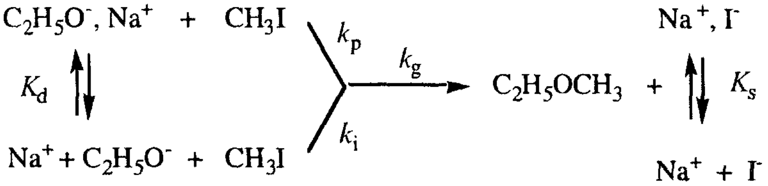
pairs. Equation (1), predicting a linear relationship between k_g and α, expresses the well known dilution effect, which is often referred to as the dual hypothesis.(7)

Generally, the dependence of reaction rate on solvent composition for nucleophilic substitution reactions in mixed solvents may give information concerning preferential or specific solvation of ionic species. Thus, in previous papers we studied the kinetics of the reaction of sodium ethoxide and methyl iodide [Eq. (2)] in ethanol–dioxane solvent systems,(5,6) where the mixture of two organic solvents, in various proportions, enabled us to change the physical properties of the reaction media.



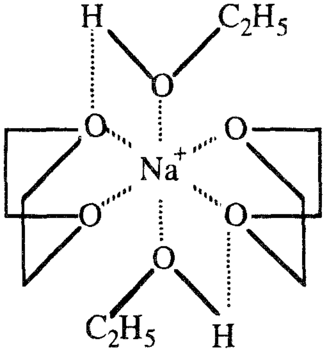
$$\begin{tikzcd} C_2H_5O^-, Na^+ + CH_3I \arrow[d, shift left] \arrow[dr, "k_p"] & & Na^+, I^- \arrow[d, shift left] \\ & {} \arrow[r, "k_g"] & C_2H_5OCH_3 + \\ Na^+ + C_2H_5O^- + CH_3I \arrow[u, shift left, "K_d"] \arrow[ur, "k_i"'] & & Na^+ + I^- \arrow[uu, shift left, "K_s"'] \end{tikzcd}$$

(2)

In these previous investigations, in agreement with analogous literature data,(8) we observed that k_g is markedly increased as the dielectric constant D of the medium progressively decreases with increasing the dioxane content. However, taking into account that the reactivity of the ion-pairs is lower than that of the free ions(9) and that the decrease of D favors the ionic association, this behavior has been explained by assuming that the non-electrostatic solute–solvent interactions are more important than the electrostatic ones. Thus, we assumed that the very poor cation-solvating ability of pure dioxane(10–12) is enhanced in mixed ethanol–dioxane mixtures by the formation of 1:1 polar complexes between dioxane and ethanol; the formation of such complexes has been detected in previous investigations.(13,14) By analogy with a model proposed by Grunwald *et al.*, concerning the specific solvation of alkali cations in water–dioxane mixtures,(15) we also assumed that Na^+ cations are probably solvated in ethanol–dioxane mixtures as is indicated in Eq. (3).

Consequently, the specific solvation of the cations leads to the formation of more "loose" ion-pairs, these species being more reactive than the "tight" ion-pairs. The final result is an important augmentation of k_g as the dielectric constant D of the medium progressively decreases, the dissociation constant K_d, contrary to the predictions of the electrostatic theory, also increases.

In an attempt to supply further evidence for the above mentioned assumptions, we decided to extent our kinetic studies to binary ethanol–cyclohexane solvent systems, where the possibility of formation of polar associates between ethanol and cyclohexane through hydrogen bonds does not exist. In these mixtures, the effect of the solvent composition on the rate constant k_g is expected to be principally of electrostatic nature. It is noted that the replacement of dioxane by cyclohexane does not greatly affect the dielectric constant of the mixtures, these organic co-solvents have similar values of D ($D_{\mathrm{diox}} = 2.203$, $D_{\mathrm{cycl}} = 2.023$ at 25°C).


(3)

However, one problem, generally encountered in such studies, is to correlate reaction rate data with the physical properties of the corresponding media. For this reason, in a recent study we examined some physical properties (density, viscosity, dielectric constant and refractive index) of ethanol–cyclohexane mixtures over the whole composition range and temperatures from 15 to 35°C.(16) This investigation evidenced changes in the self-association of ethanol with changing composition.

2. EXPERIMENTAL

2.1. Reagents

Absolute ethanol (Fluka, p.a.) was further purified according to a recommended method.(17) Cyclohexane (Merck GR > 99.5%, bp = 80.7°C/760 mmHg) was refluxed and then fractionally redistilled. In all distillations only the middle fraction coming over at the reported boiling point and comprising about 75% was retained. Solvent mixtures were gravimetrically prepared on a Mettler analytical balance. Fluka methyl iodide (puriss. p.a. > 99.5%, bp = 42–43°C/760 mmHg) was used without further purification. Sodium ethoxide was prepared from absolute ethanol and metallic sodium (BDH > 99.8%) as described previously.(6)

2.2. Measurements

The kinetics of the reaction were followed point by point. Each point corresponds with one independent experiment, performed in a tube hermetically closed containing 50 ml of the reaction solution. After a time t the content of the tube was poured in a biphase mixture of distilled water and petroleum ether. The formed NaOH in the aqueous phase was determined, at least in five replicates, by classical acidimetric titrations and the results were averaged. The titrant was a solution of H_2SO_4 prepared from stock solutions of known concentration (Merck Titrisol). In all titrations, the titrant was added to the working solution from a piston burette (Metrohm Dosimat) with a readability of 0.005 ml. The probable error in the concentration of the formed NaOH is estimated to be about equal to $\pm 10^{-4}$ M. In selected control experiments, the concentration of the formed NaI was also determined by potentiometric argentimetric titrations. Both these determinations reach to identical kinetic results. Kinetic experiments were performed at 25°C. Temperature was controlled within ±0.02°C by means of a Haake Ultrathermostat NBS. Equal initial concentrations of the reactants were used. It has been verified that under the experimental conditions of the present investigation, the solvolysis reaction between methyl iodide and ethanol was negligible.

3. DETERMINATION OF THE RATE CONSTANT

3.1. Theoretical

In a previous investigation,(5) it has been shown that the rate constant k_g of the following reaction performed in media of low dielectric constant does not remain constant during an independent kinetic experiment.

$$\mathrm{ROM} + \mathrm{R'X} \xrightarrow{k_g} \mathrm{ROR'} + \mathrm{MX} \tag{4}$$

So, it is not possible to use the classical relationship for a second order reaction where k_g is assumed to remain invariable. For this reason, the value of k_g at any time t (or x) has been determined previously(5,6) by solving numerically the appropriate differential equation

$$k_{g,x} = \frac{\left(\dfrac{dx}{dt}\right)}{(1 - x)(b - C_o x)} \tag{5}$$

where C_o and b are the initial concentrations of the alkali ethoxide ROM and the n-alkyl halide R'X respectively, and x is the degree of the reaction advancement defined by

$$y = xC_o \tag{6}$$

y being the consumed concentration of ROM at time t.

In order to evaluate the derivative $(dx/dt)_t$ at any time t (or x), the experimental curve $x = f(t)$ has been approximated to a polynomial model of the general form

$$x = \sum_{i=0}^{n} d_i t^i \tag{7}$$

From Eqs. (5, 6) it is possible to determine, at any time t, the values of the rate constant of Eq. (4), and estimate by extrapolation the value $k_{g,o}$ of this constant at $x = 0$. However, the accuracy of this procedure depends strongly on the adequacy of the polynomial Eq. (7) to approximate the experimental curve, this adequacy is considerably affected by random experimental errors.

This situation has encouraged us to develop a more strict and accurate method that permits one to determine directly from the experimental data the value $k_{g,o}$. Taking into account that $k_{g,o}$ is free of any possible influence of the products of the reaction, the determination of this parameter is of great importance in studies concerning the solvent effect on reaction rates.

This method is based on the fact that for $x < 0.3$ the variation of k_g with x of the reaction Eq. (2) is virtually linear.$^{(5)}$ So, the following equation may be written

$$k_g = m + nx \tag{8}$$

with

$$m \equiv k_{g,o} \tag{9}$$

Taking into account this equation, the integration of Eq. (5) gives

$$Y = (m + n)t \tag{10}$$

where

$$\text{for } C_o \neq b \quad Y = \frac{\ln(1 - x)}{C_o - b} - \frac{C_o(m + n)\cdot\ln\left(\frac{b - xC_o}{b}\right)}{(C_o - b)(mC_o + nb)} + \frac{n\cdot\ln\left(\frac{m + nx}{m}\right)}{mC_o + nb} \tag{11}$$

$$\text{and for } C_o = b \quad Y = \frac{n}{C_o(m + n)} \ln\left[\frac{m + nx}{m(1 - x)}\right] + \frac{1}{C_o}\left(\frac{x}{1 - x}\right) \tag{12}$$

Considering that $n = 0$, which means that k_g remains invariable during a kinetic experiment, Eq. (10) is reduced to the classical relationship for a second order reaction

$$Y = mt \tag{13}$$

where for $C_o \neq b$ and $C_o = b$ one obtains respectively

$$Y = \frac{1}{b - C_o} \ln\left(\frac{b - xC_o}{b(1 - x)}\right) \qquad Y = \frac{1}{C_o}\left(\frac{x}{1 - x}\right) \tag{14}$$

Equation (10) predicts a linear relationship between Y and t with a gradient equal to $(m + n)$. Alternatively, the experimental confirmation of such a correlation, using x and t data, supports the assumption that the variation of k_g with x is effectively linear. However, it appears, at first sight, that there is no way in which, without prior knowledge of m ($\equiv k_{g,o}$) and n, the Y *vs.* t data can be plotted to give a linear graph. This is possible with the iterative method proposed in this investigation.

3.2. Iterative Method for the Determination of $k_{g,o}$

This method is based on the main principles of previously proposed procedures that have been successfully used for the determination of the rate constants of various electrochemical reactions as well as of thermodynamic data of various acid–base equilibria.(18–21)

It is assumed first that the values of n lies in an interval (u, v). Let m^o be any trial value for m chosen arbitrarily from an interval (u', v') of possible value of this parameter.

Starting from this value, and taking from the interval (u, v) any value for n it is possible to obtain, by means of the experimental x and t data, the dependence $Y = f(t)$. This will approach a linear relationship to the extent where the chosen values for m and n also approach the exact values of these parameters. Hence, the best linearity which could be obtained, by means of the available experimental data and the chosen value m^o, evidently corresponds to the best approximation of the exact value of the parameter n. Thus, by seeking the value of n within the interval (u, v), it is possible to obtain, by means of Eq. (10), N relationships $Y = f(m^o, t)$, N being the number of the values of n taken for these calculations. For each of these relationships, the calculation by appropriate formulae(20) of R^2 (square of the correlation coefficient), F_{st} (F-statistic), and S_{yx} (standard error of estimate), permits us to examine the adequacy of the fit of Eq. (10) to the experimental x, t data. These statistics may reach a maximum (R^2 and F_{st}) and a minimum value (S_{yx}) at a value of n equal to ${}_1n^{max}$, which can be considered as a first approximation to the exact value of n. From the slope of the corresponding to ${}_1n^{max}$ linear relationship, calculated by least squares, it is possible to deduce a better approximation to the exact value of m equal to ${}_1m^1$. This new value for m can be used to refine, from the slope of the corresponding $Y = f(t)$ dependence, the value of this parameter and repeat until it converges. In all these iterations the parameter n is taken equal to ${}_1n^{max}$. The obtained after k iterations limiting value ${}_1m^{\text{lim}}$ can also be considered as a first approximation to the exact value of m.

In a second step, starting from the value ${}_1m^{\text{lim}}$, it is possible to obtain, as before, a second approximation to the values of n and m, respectively equal to ${}_2n^{\text{max}}$ and ${}_2m^{\text{lim}}$.

This procedure can be repeated f times until the values ${}_fn^{\text{max}}$ and ${}_fm^{\text{lim}}$ converge (the criterion being less than 0.005% difference in the values of the parameters n and m, between two subsequent cycles). These values express the best approximation, which can be obtained by means of the available experimental data, to the exact values of the corresponding kinetic parameters.

It should be noted that in the determination of the parameters m and n from the linear relation (10), by means of an ordinary least squares data-fitting method (OLS), one minimizes the sum of squares of the deviations in Y rather than those in the measured values of x. This defect can fortunately be remedied by using a weighted-least squares method (WLS) reported in literature.(22) Thus, by introducing a weighted factor w_i defined by $w_i = (dY_i/dx_i)^{-2}$, one obtains

$$\text{for } C_o \neq b \qquad w_i = \left(\frac{1}{(b - C_o)(1 - x_i)} + \frac{AC_o}{b - C_o x_i} + \frac{nB}{m + nx_i}\right)^{-2} \tag{15}$$

where

$$A = \frac{C_o(m + n)}{(C_o - C_l)(mC_o + nC_l)} \quad \text{and} \quad B = \frac{n}{mC_o + nC_l} \tag{16}$$

$$\text{and for } C_o = b \qquad w_i = \frac{C_o^2(m + nx_i)^2(1 - x_i)^4}{(m + n)^2} \tag{17}$$

3.3. Application of the Iterative Method for the Determination of $k_{g,o}$ Using Simulated and Experimental Data

To establish the reliability of the proposed procedure, first it must be shown that it actually works by comparison to a system where the answer is already known. Experimentally, this implies that the proposed approach, applied to an already reported system, gives a reasonable (or even better) precision on the extraction of the sought parameters. In this respect, it was considered necessary to test the proposed methods, first with simulated data corresponding to various values of C_o, b, m and n and second to experimental data resulting from a reaction between alkali ethoxide and n-alkyl halide realized in solvents of low dielectric constant.

Ideal simulated x and t data have been derived from Eq. (10). In all these calculations we assumed that $m \equiv k_{g,o} = 0.0782$ L-mol^{-1}-min^{-1}, $n =$

0.0587 L-mol^{-1}-min^{-1} and $C_o = b = 0.20M$. The results obtained are reported in Table I. It is now examined whether it is possible by means of the proposed method and using these x, t data to extract the above mentioned values of m and n.

Assuming first that k_g remains invariable, it is possible to obtain from Eq. (13) an initial estimation for m equal to $m_o = 0.08516$. It is noted that the application of the classical formulation of a second order reaction reached to a nearly linear relationship between Y and t ($R^2 = 0.9974$). Starting from this initial estimation for m, the application of the proposed method converges to the desired values of m and n after four cycles of successive approximations. The obtained sequences $\{{}_f n^{\max}\}$ and $\{{}_f m^{\lim}\}$ are summarized in Table II. The convergence to the true values $m = 0.0782$ and $n = 0.0587$ is evident. It should be noted that in all cases the graphs $R^2 = f(n)$ and $S_{yx} = f(n)$ presented respectively a pronounced maximum and minimum, as it is shown by the examples given in Fig. 1.

It should be noted that the proposed technique converges to the desired values of m and n, even in the case where one starts from very poor initial estimate of m. In an attempt to generalize the conclusions concerning the applicability of the proposed method, the total procedure was also applied in various simulated kinetic data corresponding to various values of C_o, b, m and n. In all cases it was found that this method is fairly applicable.

Table I. Ideal and Monte Carlo (M-C) Data and Experimental Kinetic Data for the Reaction $C_2H_5ONa + CH_3I$ Realized in Ethanol–Dioxane Systems Containing 10% by Volume Dioxane[a]

	x		t (min)	x
t (min)	Ideal data[b]	M-C data[c]	Experimental data[d]	
1.96	0.0300	0.0300	6.23	0.0741
3.99	0.0600	0.0596	9.18	0.1071
6.11	0.0900	0.0896	12.85	0.1463
8.33	0.1200	0.1206	16.37	0.1819
10.66	0.1500	0.1490	19.10	0.2083
13.11	0.1800	0.1779	22.00	0.2351
15.69	0.2100	0.2109	24.26	0.2551
18.43	0.2400	0.2410	28.80	0.2930
21.33	0.2700	0.2715		
24.42	0.3000	0.2991		

[a] For ideal and Monte Carlo data ($C_o = b = 0.20$ M, $m = 0.0782$ L-mol^{-1}-min^{-1}, $n = 0.0587$ L-mol^{-1}-min^{-1}). For experimental kinetic data ($C_o = 0.0972$ M, $b = 0.10$ M).

[b] Values that exactly fit Eq. (10).

[c] Mean values of six normally distributed deviates generated from the ideal data with coefficient of variation equal to 2%.

[d] Data taken from Ref. 5.

Table II. Successive Approximations to m and n Values Obtained by Means of the Proposed Iterative Method and the Data of Table I

f	${}_{f}n^{\max}$	${}_{f}m^{\lim}$	${}_{f}n^{\max}$	${}_{f}m^{\lim}$	${}_{f}n^{\max}$	${}_{f}m^{\lim}$
	Simulated data					
	Ideal data		Monte Carlo data		Experimental data	
1	0.0650	0.0775	0.0700	0.0769	0.1400	0.1219
2	0.0575	0.0783	0.0625	0.0778	0.1225	0.1239
3	0.0587	0.0782	0.0625	0.0778	0.1238	0.1237
4	0.0587	0.0782			0.1238	0.1237

The examples studied previously showed that the proposed procedures are able to extract m and n values in the particular case where the used x and t data are free of experimental errors.

However, of more experimental interest is the question of how well the new technique is able to cope with kinetic data containing random extraneous contributions, such as annoying experimental "noise." To investigate this, a Monte Carlo technique was used, which has been detailed in a previous paper(18) and need not be repeated here. The main idea of this procedure is based on the observation that, often, random experimental errors closely follow a Gaussian (or normal) distribution. Thus, at each point (t_i and x_i) of the theoretical kinetic curve $x = f(t)$, we produced a number N of normally distributed random variables $x_{i,j}$ with mean x_i and

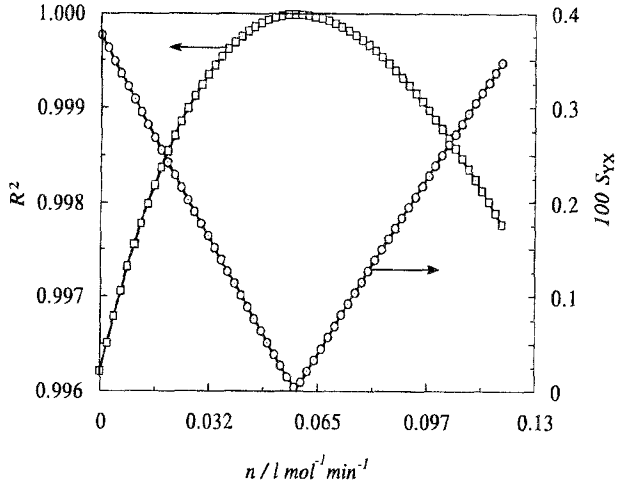


Fig. 1. Variation of R^2 and S_{yx} with n during the last cycle (f = 4) of successive approximations on the simulated kinetic data of Table I.

standard deviation S_i. In the experimental level, this implies the determination of x in N replicates with a precision equal to S_i. Using this technique, we treated again, as an example, the simulated kinetic data reported in Table I. In this treatment we assumed that the coefficient of variation $[(S_i/x_i)100]$ is equal to 2%. At each time t_i, we created six values of $x_{i,j}$ and the results were averaged. The mean values $\bar{x}_{i,j}$ are summarized in Table I. Evidently, these values would coincide with the corresponding x_i values only in the case where the number N of the produced random variables $x_{i,j}$ tends to infinity. Using these Monte Carlo (M-C) data $\bar{x}_{i,j}$, the proposed method gives the values $m = 0.0778$ and $n = 0.0625$. These results are respectively within 0.56% and 6.5% of their true magnitudes. Evidently, the proposed technique is able to extract the value of $k_{g,o}$, with an accuracy much better than the supposed experimental error of the kinetic data (=2%). To the contrary, in all instances examined in this investigation it was found that the n values obtained are considerably affected by random experimental "noise;" the uncertainty of these values being much greater than the corresponding experimental error. So, the accurate determination of n ($= dk_g/dx$) requires very precise kinetic data. However, the determination of this parameter is out of the scope of the present investigation.

It should be noted that the application of the proposed method to various M-C data showed that this procedure always reach to more accurate results, in comparison with the results of the previously reported numerical method for the determination of $k_{g,o}$.(5)

The proposed methodology was also applied on experimental data. For this purpose the previously reported kinetic data(5) for the reaction between C_2H_5ONa and CH_3I, realized in ethanol–dioxane systems containing 10% by volume dioxane ($C_o = 0.0972M$, $b = 0.10\ M$), have been treated again by means of the present iterative method. The previously proposed numerical procedure(5) for the determination of $k_{g,o}$ reached to the following relationship

$$k_g = m + nx = 0.1241 + 0.1218x \qquad (18)$$

As previously, the initial estimation for m, equal to $m^o = 0.1382$, has been determined from Eq. (13); the corresponding relationship $Y = f(t)$ being nearly linear ($R^2 = 0.9956$). Starting from this initial estimation for m, the application of the proposed method converges, after four cycles of successive approximations, to the values

$$m = 0.1238\ \text{L-mol}^{-1}\text{-min}^{-1} \text{ and } n = 0.1237\ \text{L-mol}^{-1}\text{-min}^{-1}.$$

These values are evidently very close to the coefficients of Eq. (18).

4. RESULTS AND DISCUSSION

Table III summarizes the %*v*/*v* compositions of all the binary cyclohexane + ethanol solvent systems used in this investigation and also gives the corresponding values of the mole fraction x_2 of cyclohexane. A statement that the %*v*/*v* composition of a binary solvent is, for example, 20% cyclohexane means that this system was prepared by mixing 20 ml of cyclohexane with ethanol up to a final volume of 100 ml. Table III also contains the corresponding values $k_{g,o}$ of the reaction

$$C_2H_5ONa + CH_3I \rightarrow C_2H_5OCH_3 + NaI \qquad (19)$$

From the values of Table III the following remarks can be deduced:

1. At each solvent composition, $k_{g,o}$ is found to increase with decreasing the alkoxide concentration C_o. This is the well known dilution effect, which becomes progressively less important as the cyclohexane content increases.

2. At each value of C_o, the rate constant $k_{g,o}$ increases with increasing dielectric constant of the medium.

Table III. Values of $k_{g,o}$ for the Reaction $C_2H_5ONa + CH_3I$ as a Function of the Concentrations of Sodium Ethoxide and the Solvent Composition at 25°C

C_o^a	$10^3k_{g,o}^b$	C_o	$10^3k_{g,o}$	C_o	$10^3k_{g,o}$
10% *v*/*v* Cyclohexane		20% *v*/*v* Cyclohexane		30% *v*/*v* Cyclohexane	
$x_2 = 0.0565^c$		$x_2 = 0.1188^c$		$x_2 = 0.1894^c$	
$D = 22.204^d$		$D = 19.719^d$		$D = 17.100^d$	
0.0997	73.0±0.5	0.0991	61.1±0.1	0.0998	48.4±0.3
0.1452	69.8±0.1	0.1484	57.6±0.2	0.1505	45.7±0.1
0.1994	66.7±0.2	0.1982	54.9±0.4	0.1996	43.7±0.3
0.2486	64.8±0.4	0.2465	53.0±0.3	0.2495	42.3±0.1
0.2904	63.7±0.4	0.2968	51.7±0.1	0.3010	41.3±0.3
40% *v*/*v* Cyclohexane		50% *v*/*v* Cyclohexane			
$x_2 = 0.2674^c$		$x_2 = 0.3539^c$			
$D = 14.423^d$		$D = 11.708^d$			
0.0987	37.9±0.3	0.0991	32.0±0.2		
0.1488	35.7±0.3	0.1500	29.8±0.2		
0.1975	34.0±0.2	0.1982	28.3±0.1		
0.2463	32.8±0.1	0.2458	27.2±0.3		
0.2976	32.1±0.1	0.3000	26.4±0.1		

[a] Concentration of sodium ethoxide; units: mol-L^{-1}.

[b] Units: L-mol^{-1}-min^{-1}.

[c] x_2 = mole fraction of the cyclohexane.

[d] Dielectric constant of the solvent mixtures taken from Ref. 16.

The above remarks are in accordance with Acree's dual hypothesis. Indeed, at constant solvent composition, as C_o increases, the dissociation of the ion-pairs decreases lowering the rate constant of the reaction. On the other hand, the decrease of D favors the formation of ion pairs which are less reactive than the unassociated nucleophilic anions.

However, the reduction of $k_{g,o}$ produced by progressively increasing the cyclohexane content cannot be exclusively ascribed to changes in dielectric constant of the solvent medium. Other factors, such as the various non-electrostatic solute–solvent interactions (e.g., solvation of various reactant species), presumably contribute to the changes in the rate constant after a change of the solvent composition. Assuming that further information about these effects might be supplied by examining the dependence of k_i, k_p and K_d (reaction Eq. (2)) on the solvent composition, these parameters have been determined, by means of a method described previously,(2) exclusively from the kinetic data of Table III. The obtained results are given in Table IV along with the *%v/v* cyclohexane content.

The variation of k_i with solvent composition (Table IV) reflects the decrease of the reactivity of $C_2H_5O^-$ with the addition of cyclohexane. Taking into account that the strongly solvated species are less reactive than the poorly solvated ones,(8,23,24) it is believed that the decrease of k_i with the addition of cyclohexane is a result of the enhancing ability of ethanol to solvate anions rather than inhibition by cyclohexane. Indeed, it is well known for a long time that anions are preferentially solvated by hydroxylic solvents through hydrogen bonds(8,10,23,24) and that alcohols in solutions in nonpolar solvents associate through hydrogen bonds into a series of *n*-meres.(16,25,26) In very dilute solutions the predominant species are the unassociated (monomeric) molecules, while in concentrated solutions of alcohols only linear *n*-meres can be considered. In addition, it has been postulated that, in pure alcohols or in concentrated solutions of these substances in nonpolar liquids, the formed linear *n*-meres present a higher dipole moment. This behavior has been attributed to the fact that the O–H bond moment of these aggregates is

Table IV. Values of k_i, k_p, and K_d of the Reaction $C_2H_5ONa + CH_3I$ as a Function of the *%v/v* Cyclohexane Content at 25°C

%v/v	D^a	10^3k_p	10^3k_i	10^3K_d
10	22.204	39.6	107.1	13.7
20	19.719	29.6	98.9	10.0
30	17.100	25.8	80.1	7.06
40	14.423	19.9	66.5	5.47
50	11.708	15.2	60.1	4.52

[a] Values of the bulk dielectric constant of the solvent mixtures taken from Ref. 16.

increased through mutual induction.(10,16,25) However, when the nonpolar solvent is added, these associates are broken up and the resulting hydrogen-bonded species have a lower dipole moment. Consequently, the addition of cyclohexane, promoting the depolymerization of alcohol, increases the fraction of monomeric molecules. On the other hand, it has been argued in literature that these monomeric molecules enhance the ability of alcohol to solvate large organic ions with low density of surface charge.(27)

It is worth noting that in the case of ethanol–dioxane mixtures, where the produced monomeric molecules of ethanol were consumed in order to form with dioxane hydrogen-bonded polar associates, the reaction rate k_i remained constant, independently of the dioxane content.(6)

The values of Table IV show that k_p falls as the the concentration of cyclohexane is increased. This behavior may be attributed to the presence of two species: (a) less reactive contact ion pairs (CIP) and (b) much more reactive solvent separated ion pairs (SSIP). Assuming also, in accordance with literature,(10) a rapid equilibrium between CIP and SSIP, we can rationalize our results by considering that the addition of cyclohexane, decreasing the dielectric constant of the solvent mixture, shifts this equilibrium in favor of the contact ion pairs.

Indeed, it has been postulated many years ago(28,29) that the association of free ions into ion pairs may involve a stepwise process involving two kinds of ion pairs (CIP, SSIP). The first step would be formation of an ion pair in which either one or both ions essentially retain their solvation shell. A still closer approach of the two ions would then necessitate at least a partial desolvation of the ions requiring a substantial amount of energy. The increase in Coulombic attraction on the formation of the contact ion pair as well as the gain in entropy on desolvation would constitute the driving force for this reaction. Consequently, taking into account the above remarks, we can consider that in solutions of C_2H_5ONa in pure ethanol both CIP and SSIP coexist, while in solutions of this alkoxide in a nonpolar solvent, such as cyclohexane, the predominant species are the CIP. Thus, the addition of cyclohexane, increasing the Coulombic attraction between anions and cations, also increases the amount of CIP. On the other hand, as the Coulombic attraction increases, SSIP become more tight; the tighter the ion pair the smaller its reactivity.

In addition to the above remarks, it is noted that the depolymerization of ethanol, produced by the addition of cyclohexane, is accompanied by the presence in the solution of species of lower dipole moment. However, in discussing the solvation of small metal ions in mixed organic solvents, one of the most common assumptions is that the ions are surrounded predominantly by the molecules of the more polar solvent. In accordance with this assumption, it is reasonable to consider that the forces contributing to Na^+ solvation in mixed cyclohexane–ethanol mixtures are of electrostatic nature (ion–dipole interactions). Consequently, the addition of cyclohexane decreasing the medium polarity, designated by the dipole moment of its molecules, decreases the ability of the solvent mixture to solvate the cations. Evidently, in such a case, the amount of the ion desolvation energy required for the formation of CIP is reduced.

Finally, the significant decrease of K_d, demonstrated by the values of Table IV, attending the lowering of the dielectric constant of the solvent medium indicates that the solvent effect on this constant is principally of electrostatic nature.

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