

Molecular Organization of Reagents in the Kinetics and Catalysis of Liquid-Phase Reactions: XI. Manifestation of the Structure of Solution in the Kinetics of Water Addition to Isocyanate in Water–Dioxane Mixtures

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Abstract—Evidence for the structural effect of liquids associated by hydrogen bonds on the kinetics of molecular reactions was experimentally found. The kinetics of hydrolysis of (phenylaza)phenyl isocyanate in water–dioxane mixtures was studied at various temperatures and in the presence of structure-making and structure-breaking additives. The apparent order γ of reaction with respect to water concentration increased with temperature because of the partial breaking of the H-bond solution structure. It was found that the value of γ was affected by salt additives, for which positive (Et_4NCl) or negative (KI) hydration is typical. This hydration resulted in strengthening or partially breaking the H-bond structure of water, respectively. It follows from the kinetic data that the addition of 0.1 mol/l Et_4NCl was equivalent to a decrease in the solution temperature by 6 to 7°C, whereas the addition of 0.1 mol/l KI was equivalent to an increase in the temperature by 5 to 6°C. The effect of poly(ethylene oxide) additives (which stabilize the structure of water) on the value of γ was similar to the effect of the tetraethylammonium salt, which is characterized by positive hydration.

INTRODUCTION

The quantitative consideration of the molecular organization of a medium in the kinetics of reactions that occur in solutions associated by hydrogen bonds is a weakly developed area of chemical kinetics. In many cases, a reactant that is capable of enhancing the structure of a liquid by H-bonds is simultaneously a constituent of a mixed solvent. The apparent reaction rate constant is a complicated function of concentration of this reactant in the system; this complicated function reflects changes in the molecular organization of the medium depending on its composition. Only at low reactant concentrations, which provide an opportunity to experimentally determine the concentrations of various self-associates and heteroassociates in the system, can the kinetics of liquid-phase reactions be successfully described, albeit in relatively inert solvents (for example, see [1–3]). The specific structural organization of associated solutions should be taken into account in the quantitative interpretation of the concentration dependence of apparent rate constants over the entire range of medium compositions in solvents of different chemical nature. We considered this problem in detail previously [4–6]. In the cited publications, we developed a new approach to liquid-phase reactions in associated media. This approach is based on the consideration of these media as pseudopolymer systems and on analogies between the behaviors of the chain associates of aliphatic alcohols, which are formed by hydro-

gen bonds, and flexible chain macromolecules in solutions.

In contrast to polymer chains, whose units are linked by covalent bonds, linear alcohol associates in solutions occur as short-lived pseudopolymer chains. By analogy with the behavior of real macromolecules in solutions, it is believed that H-bond chains can roll themselves into coils. Upon attaining a so-called critical concentration C_{cr} , the coils overlap with the formation of a three-dimensional physical network of hydrogen bonds. The structural elements of this network are polymolecular clusters of H-bond alcohol molecules; in this respect, they are analogous to so-called flickering clusters of water molecules.¹ The notion of flickering clusters is used in the description of the structure of aqueous solutions [7].

In terms of the developed approach to associated solutions as pseudopolymer systems, the relationship between the cluster size r and the concentration of H-bound constituent molecules (C) at $C > C_{\text{cr}}$ should be expressed as the power function, which is analogous to the law that relates the size of a polymer coil in solution

¹ The term *flickering clusters* is used in the theory of aqueous solutions for the interpretation of physicochemical properties, which requires notions of the occurrence of loose (short-lived H-bond clusters of water molecules) and closely packed (monomeric water molecules) regions, which are in a thermodynamic equilibrium with each other, in a liquid structure [7].

to the concentration of covalently bound monomer units [8],

$$r \sim (C/C_{cr})^{-\gamma}. \quad (1)$$

The exponent of power γ depends on the thermodynamic quality of solvent² ω as $\gamma = \omega/(3\omega - 1)$ [8]. The value of ω is related to the so-called Flory interaction parameter χ , which is a combination normalized to kT , of the energy of intermolecular interaction of monomer units with solvent molecules, the energy of noncovalent bonding of monomer units with each other, and the energy of interaction of solvent molecules with each other [9].

At $C > C_{cr}$, associated solutions are in reality microheterogeneous systems. If a chemical reaction with the participation of the OH groups of corresponding clusters takes place in such a structured medium in a considerable excess of an alcohol or water over the concentration of the second reactant, this reaction occurs on crossing the cluster surface by the reactant [4, 5]. In this case, the apparent pseudo-first-order rate constant (k_a) is proportional to the concentration and the surface area of clusters. Because the concentration of clusters is inversely proportional to their volume $1/r^3$ and the area is proportional to r^2 , taking into account Eq. (1), we obtain

$$k_a \sim 1/r \sim (C/C_{cr})^{\gamma}. \quad (2)$$

The exponent of power γ formally corresponds to the apparent order of reaction at $C > C_{cr}$, and its value is sensitive to whether a given medium enhances the stabilization of an H-bond chain structure or destroys it.

Previously [6, 10], addition reactions with the participation of aliphatic alcohols, which simultaneously acted as solvent components, were considered as an example. It was found that the parameter γ increased on going from solvents in which the H-bond chains of alcohol molecules and the corresponding clusters are reasonably stable (structure-keeping solvents) to solvents breaking the H-bond liquid structure (structure-breaking solvents). An increase in the temperature exerted a similar effect on the value of γ because of the degradation of polymolecular associates [4].

In this work, we attempted to extend the developed concept of the role of a medium in the kinetics of molecular reactions in H-bond systems to processes occurring in binary solutions one of the components of which is water. In this case, along with varying the tem-

² In this case, we use terminology accepted in the physical chemistry of polymer solutions [8, 9]. A solvent in which the energy of interaction between units that form a polymer chain and solvent molecules is greater than the energy of noncovalent interaction of units with each other is referred to as a thermodynamically good solvent. The opposite situation occurs in a thermodynamically poor solvent for a polymer chain. The so-called θ -solvent is characterized by the equality of the corresponding energies of intermolecular interaction. Previously [6], we critically discussed the applicability of polymer terminology to the description of the behavior of H-bond chains in solutions.

perature, additives favorable (because of special features of their solvation) to the stabilization or partial degradation of the H-bond water structure were introduced into the system. The hydrolysis of (phenylazla)phenyl isocyanate in aqueous dioxane was studied as a model reaction. Under ordinary conditions, this is a multistep process at comparable reactant concentrations. At the first (slow) step, water is added to isocyanate to form a carbamic acid: $R-N=C=O + H_2O \Rightarrow R-NHCOOH$. This latter almost instantaneously decomposes into CO_2 and RNH_2 . Next, the resulting amine reacts with the parent isocyanate to form a substituted urea (RNH_2CO) [11].

Previously [12], it was found that the kinetics of the rate-limiting step of hydrolysis, that is, the step of water addition to the NCO group of an isocyanate, can be studied when the reaction is performed in a large excess of water at an isocyanate concentration of about 10^{-5} mol/l. These conditions were used in this work in a spectrophotometric study of the reaction kinetics in aqueous dioxane over a temperature range of 12–50°C. The reaction occurred directly in a quartz cuvette of a Specord UV–VIS or Specord M40 spectrophotometer. The cuvette was thermostatted to within 0.5°C. The course of the reaction was monitored by measuring the absorbance of the initial isocyanate at a wavelength of 240 nm. The concentration of water in dioxane was varied within a range of 3–20 mol/l, that is, at $C > C_{cr}$ [4–6]. In this large excess of water, the reaction was of pseudo-first order with respect to isocyanate up to 100% conversion. Dioxane was purified to remove peroxides and dried in accordance with the published procedure [13]. Water was twice distilled in a quartz apparatus. The salts used as additives, tetraethylammonium chloride (Et_4NCl) and potassium iodide (KI), were recrystallized from aqueous solutions. Poly(ethylene oxide) of molecular mass 20000 from Merck was used without additional purification.

The aim of this study was to obtain the concentration dependence of the apparent rate constant at various temperatures and in the presence of additives that affect the structure of solution, to treat these functions using Eq. (2), and to calculate the parameter γ , which characterizes the sensitivity of this reaction to changes in the molecular organization of the medium, in accordance with the developed model.

RESULTS AND DISCUSSION

Figure 1 demonstrates the apparent rate constants as functions of water concentration at different temperatures plotted in bilogarithmic coordinates in accordance with Eq. (2) at $C = [H_2O]$. The table summarizes the values of γ for the given reaction, which were calculated from the slopes of the corresponding straight lines. It can be seen that γ changed by a factor of about 1.5 within the tested range of temperatures. As the temperature was increased, γ increased because of liquid structure breaking, as was the case in analogous addi-

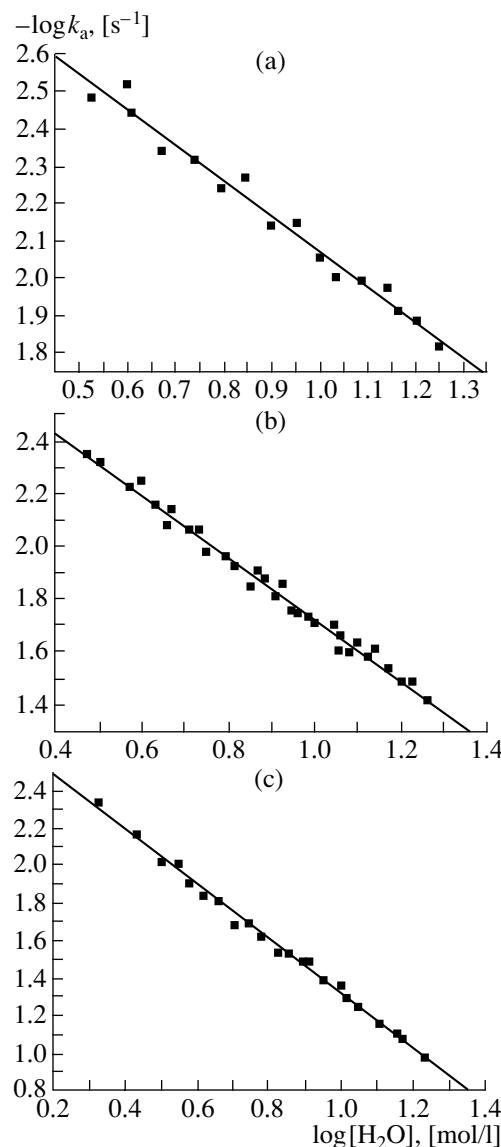


Fig. 1. Bilogarithmic plots of the concentration dependence of the apparent rate constant of (phenylaza)phenyl isocyanate hydrolysis in water-dioxane mixtures at (a) 12, (b) 28, and (c) 50°C.

tion reactions with the participation of aliphatic alcohols, which were present as the constituents of a medium [4]. However, this effect was much more pronounced in the case of aqueous solutions. Note that the noninteger values of the exponent of power γ , which formally corresponds to the order of reaction with respect to water, provide indirect evidence for the fractal structure of H-bond clusters taking part in the reaction [10, 14].

It is well known that many physicochemical properties (which depend on the special features of H-bond liquid structures) of water and aqueous solutions undergo changes in the presence of various salt additives [15]. These changes are based on the phenomena

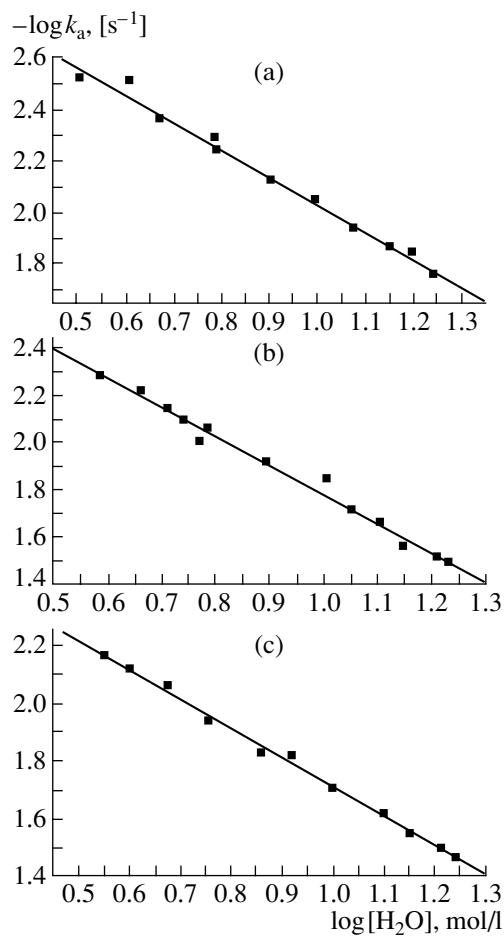


Fig. 2. Bilogarithmic plots of the concentration dependence of the apparent rate constant of (phenylaza)phenyl isocyanate hydrolysis in water-dioxane mixtures at 28°C in the presence of the additives of (a) Et_4NCl , (b) KI, and (c) poly(ethylene oxide).

of positive and negative hydration, the concept of which was first introduced as early as the 1950s by Samoilov [16]. The influence of ions on the translational motions of the nearest water molecules breaks the liquid structure. In this case, salts that are characterized by positive hydration stabilize the H-bond structure of water, whereas salts that are characterized by negative hydration destroy this structure [15, 16].

In this work, we studied the kinetics of the model reaction of (phenylaza)phenyl isocyanate hydrolysis in the presence of Et_4NCl and KI additives, which are characterized by positive and negative hydration, respectively [15], from the standpoint of the effect of the type of hydration on the structure of aqueous solutions. Unfortunately, limited solubility in aqueous dioxane allowed us to study the reaction kinetics at salt concentrations no higher than 0.1 mol/l, and we could not expect great changes in the parameter γ . At the same time, as can be seen in Figs. 2a and 2b and in the table, γ indeed changed compared with the reaction in the

absence of salts at the same temperature (28°C). These changes were distinctly higher than the standard error of the determination of γ from kinetic data.

It follows from the above results that the directions of changes in γ in the presence of the tested additives exactly correspond to the role of positive or negative hydration in the stabilization or partial degradation of the H-bond structure of a liquid. Thus, a decrease in γ in the presence of Et_4NCl (positive hydration) is analogous to the effect of a decrease in temperature, which results in the ordering of the solution structure. It is well known [15] that the solvation shells formed around tetraalkylammonium salts Alk_4NX exhibit an icelike structure, which is characteristic of the H-bond network of water. Jolicoeur *et al.* [17] found that changes in the NIR spectrum of water, which appeared upon the addition of 0.2–1.0 mol/l Bu_4NBr , were quantitatively consistent with changes observed in the spectrum upon a decrease in the temperature by 13°C. As can be seen in Fig. 3 (indicated by arrows), a decrease in γ from 1.17 to 1.08 in the presence of Et_4NCl corresponds to a decrease in the temperature by ~6 to 7°C. In the presence of KI, a salt characterized by negative hydration, the parameter γ increased up to 1.25, which corresponds (indicated by an arrow in Fig. 3) to an increase in the temperature by 5 to 6°C.

Aqueous solutions can be additionally structured by the addition of hydrophilic polymers such as poly(ethylene oxide), because of the special features of the solvation of macromolecular chains. Each ethylene oxide group of the poly(ethylene oxide) molecule is strongly solvated with three water molecules [18, 19]. In this case, the macromolecular chain becomes incorporated into the structure of water; it is likely that this structure is additionally strengthened because of hydrophobic interactions. If the H-bond solution structure is strengthened in the presence of poly(ethylene oxide), the parameter γ is changed in the same direction as with additives of the tetraethylammonium salt, which is characterized by positive hydration. In this work, we studied the kinetics of (phenylaza)phenyl isocyanate hydrolysis in the presence of relatively high-molecular-weight ($M = 20000$) poly(ethylene oxide), and, as follows from Fig. 2c and the table, the direction of the change of γ is consistent with the expectation. It follows from the value $\gamma = 1.02$ (see the table) that the poly(ethylene oxide) additive is equivalent to a decrease in the temperature (indicated by an arrow in Fig. 3) by 10–11°C in the effect on the structure of a water–dioxane solution.

In conclusion, note that although the liquid structure enhancing and breaking effects observed in this study are moderately high (except the effects due to temperature changes), they are distinctly higher than the conceivable errors of kinetic experiments, which are given as standard deviations in the last column of the table. In the context of the role of molecular organization in associated solutions, studies of the kinetics of reactions

Parameters γ in the reaction of (phenylaza)phenyl isocyanate hydrolysis in water–dioxane mixtures at various temperatures and in the presence of structure-making and structure-breaking additives

$T, ^\circ\text{C}$	Additive, mol/l	γ	R^*	S^{**}
12	–	0.94	0.991	0.036
28	–	1.17	0.994	0.024
50	–	1.45	0.997	0.024
28	KJ, 0.1	1.25	0.995	0.038
28	$\text{Et}_4\text{NCl}, 0.1$	1.08	0.996	0.032
28	Poly(ethylene oxide), 3×10^{-3}	1.02	0.999	0.016

* Coefficient of correlation.

** Standard deviation.

in ultrasonic fields below a cavitation threshold under conditions that prevent kinetic changes due to temperature effects seem promising. A few studies on this subject matter have been reported [20]; however, most attention was focused on the interpretation of changes in the apparent rate constant under ultrasonication. The results of this study and the developed theoretical model of molecular reactions in associated media [4–6, 11] suggest that the structurization or structure degradation of a liquid will affect the concentration dependence of the apparent rate constant rather than the rate constant itself.

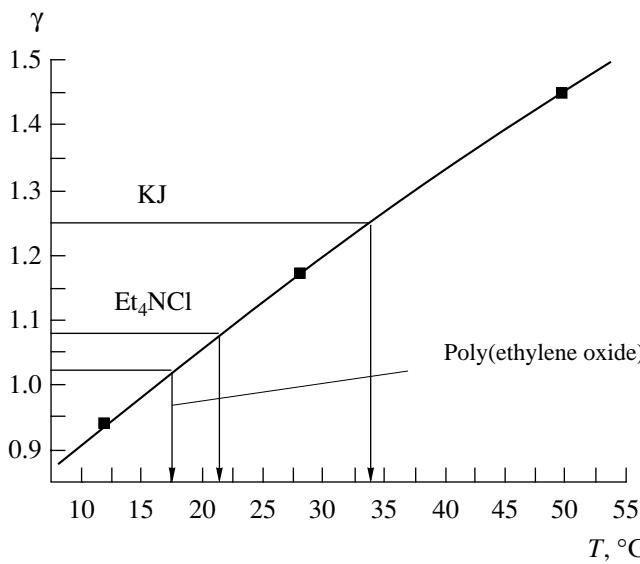


Fig. 3. The temperature dependence of the exponent of power γ in Eq. (2).

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REFERENCES

1. Bondarenko, S.P., Chirkov, Yu.N., Tiger, R.P., *et al.*, *Kinet. Katal.*, 1989, vol. 30, no. 3, p. 599.
2. Bondarenko, S.P., Zaporozhskaya, S.V., Tiger, R.P., *et al.*, *Khim. Fiz.*, 1986, vol. 5, no. 11, p. 1538.
3. Berlin, P.A., Bondarenko, S.P., Tiger, R.P., *et al.*, *Khim. Fiz.*, 1984, vol. 3, no. 5, p. 722.
4. Tiger, R.P., Tarasov, D.N., and Entelis, S.G., *Khim. Fiz.*, 1996, vol. 15, no. 11, p. 11.
5. Tarasov, D.N., Tiger, R.P., Entelis, S.G., *et al.*, *Kinet. Katal.*, 1997, vol. 38, no. 4, p. 516.
6. Tarasov, D.N., Tiger, R.P., Entelis, S.G., *et al.*, *Kinet. Katal.*, 1999, vol. 40, no. 1, p. 32.
7. Nemethy, G. and Sheraga, H.A., *J. Chem. Phys.*, 1962, vol. 36, p. 3382.
8. De Gennes, P., *Scaling Concepts in Polymer Physics*, Ithaca: Cornell University Press, 1982.
9. Flory, P., *Statistical Mechanics of Chain Molecules*, New York: Wiley, 1969.
10. Tarasov, D.N., Tiger, R.P., and Entelis, S.G., in *Polimery* (Polymers), Moscow: Inst. of Chemical Physics, 2000, vol. 2, p. 59.
11. Saunders, J. and Frisch, K.S., *Polyurethanes: Chemistry and Technology*, New York: Wiley, 1962.
12. Bekhli, L.S., Tiger, R.P., and Entelis, S.G., *Vysokomol. Soedin.*, 1969, vol. 11, no. 6, p. 460.
13. *Organic Solvents: Physical Properties and Methods of Purification*, Weissberger, A., Ed., New York: Wiley, 1955.
14. Smirnov, B.M., *Usp. Fiz. Nauk*, 1986, vol. 149, no. 2, p. 177.
15. Gordon, J.E., *The Organic Chemistry of Electrolyte Solutions*, New York: Wiley, 1975.
16. Samoilov, O.Ya., *Struktura vodnykh rastvorov elektrolytov i gidratatsiya ionov* (Structure of Aqueous Electrolytes and Hydration of Ions), Moscow: Akad. Nauk SSSR, 1957.
17. Jolicœur, C., Nguyen Dinh The, Cabana, A., *Can. J. Chem.*, 1971, vol. 49, p. 2008.
18. Liu, K.J. and Parsons, J.L., *Macromolecules*, 1969, vol. 1, p. 529.
19. Maxfield, J. and Shepherd, I.W., *Polymer*, 1975, vol. 16, p. 505.
20. *Chemistry with Ultrasound*, Mason, T.J., Ed., Amsterdam: Elsevier, 1990.