STUDY OF THE SOLVENT EFFECT IN THE AMINE EXCHANGE OF SCHIFF BASES, V.

CONNECTION BETWEEN THE RATE CONSTANT AND THE PARAMETERS E_T^N AND B_{KT} OF THE SOLVENT MIXTURES APPLIED

By

P. NAGY[*] and R. HERZFELD

Department of Chemistry, Gyula Juhász Teachers' Training College, P.O.B. 396, H-6701 Szeged, Hungary

The amine exchange of Schiff bases was studied in various solvent mixtures. With a regression equation, there was a good correlation between the rate constant and the solvent mixture parameters.

Introduction

We earlier studied the reactions of N-(2-hydroxybenzylidene)aniline and of N-(2-hydroxy-1-naphthylidene)aniline with n-butylamine and with benzylamine in ethanol-cyclohexane and in ethanol-benzene solvent mixtures [1-3]. The following correlation was found to hold between the rate constants and the activity coefficient of the ethanol in the solvent mixture [2, 3]:

$$\log k = x_1 \log k_1^* + x_2 \log k_2^* + (a_k + b_k \gamma_1) x_1 x_2 \qquad (1)$$

where k, k_1^* and k_2^* are the rate constants in the mixture, in ethanol and in the aprotic solvent, respectively; x_1 and x_2 are the respective mole fractions; a_k and b_k are constants; and γ_1 is the activity coefficient of the ethanol in the mixture. Correlations similar to (1) hold for the acidity and basicity parameters measured in these solvent mixtures [4]:

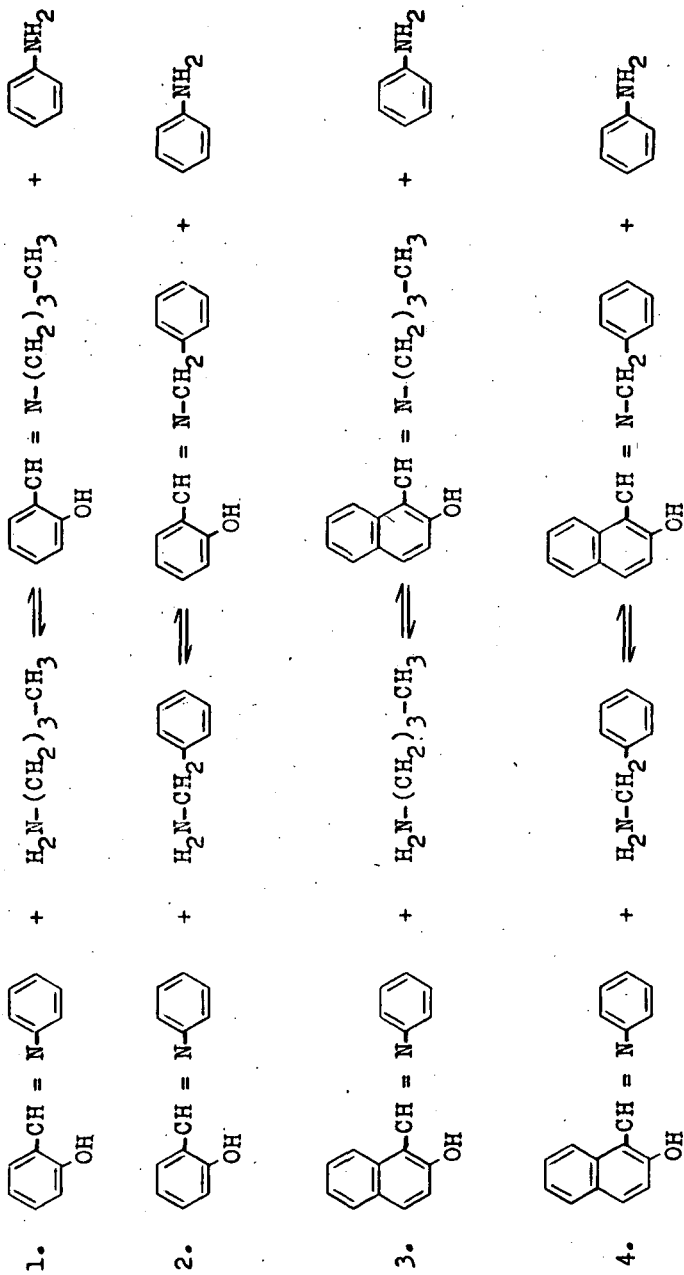$$E_T^N = x_1(E_T^N)_1^* + x_2(E_T^N)_2^* + (a_E + b_E\gamma_1)x_1x_2 \qquad (2)$$

$$B_{KT} = x_1(B_{KT})_1^* + x_2(B_{KT})_2^* + (a_B + b_B\gamma_1)x_1x_2 \qquad (3)$$

The present paper reports on a study of the correlations between the acidity and basicity parameters and the rate of the amine exchange in ethanol-n-hexane, ethanol-cyclohexane and ethanol-benzene mixtures. The results provide further data promoting a better understanding of the mechanism of the amine exchange and of the solvent effect.

Experimental

The rate constants for reactions 1-4 were determined in ethanol-n-hexane, ethanol-cyclohexane and ethanol-benzene solvent mixtures with various compositions. Measurements were performed at 25°C. The reactions were followed spectrophotometrically.

The Dimroth-Reichardt $E_T(30)$ [5] and E_T^N [6] values were used to characterize the acidity of the solvent mixtures applied. The basicity was characterized with the Krygowski et al. [7] modification of the Kamlet-Taft [8] parameter B_{KT} [4]. The solvents were purified by means of the methods customary in spectroscopy, and were carefully freed from water.

1. (salicylaldehyde–aniline Schiff base, ortho-OH) $CH=N-C_6H_5$ + $H_2N-(CH_2)_3-CH_3$ ⇌ (ortho-OH) $CH=N-(CH_2)_3-CH_3$ + $C_6H_5-NH_2$

2. (salicylaldehyde–aniline Schiff base, ortho-OH) $CH=N-C_6H_5$ + $H_2N-CH_2-C_6H_5$ ⇌ (ortho-OH) $CH=N-CH_2-C_6H_5$ + $C_6H_5-NH_2$

3. (2-naphthol Schiff base) $CH=N-C_6H_5$ + $H_2N-(CH_2)_3-CH_3$ ⇌ (2-naphthol) $CH=N-(CH_2)_3-CH_3$ + $C_6H_5-NH_2$

4. (2-naphthol Schiff base) $CH=N-C_6H_5$ + $H_2N-CH_2-C_6H_5$ ⇌ (2-naphthol) $CH=N-CH_2-C_6H_5$ + $C_6H_5-NH_2$

Results and discussion

The rate constants for reactions 1-4 in ethanol-
-cyclohexane and in ethanol-benzene were reported earlier,
as were the E_T^N and B_{KT} values for these mixtures [1, 2, 4].
The data relating to the ethanol-n-hexane mixtures are
given in Table I.

Table I

E_T^N and B_{KT} data, and the log k values for reactions 1-4 in
ethanol-n-hexane mixtures at 25°C

x_1	E_T^N	B_{KT}	log k			
			react.1	react.2	react.3	react.4
0.000	0.074*	0.00*	–	–	–	–
0.054	0.496	0.51	1.42	1.19	1.26	1.16
0.106	0.516	0.74	1.69	1.47	1.45	1.31
0.199	0.527	0.86	1.88	1.73	1.56	1.43
0.359	0.546	0.95	–	1.94	–	1.50
0.490	0.565	0.93	2.22	2.05	1.62	1.51
0.599	0.577	0.88	–	2.10	–	1.53
0.692	0.587	0.86	2.30	2.15	1.64	1.52
0.771	0.592	0.83	–	2.18	–	–
0.840	0.603	0.82	2.34	2.23	1.66	1.56
0.900	0.623	0.79	–	2.28	–	1.55
0.953	0.632	0.76	2.53	2.31	–	1.56
1.000	0.651	0.75	2.54	2.37	1.71	1.61

*Literature data [6, 7]

The literature contains a very large number of examples
of correlations between the rate constants of various reac-
tions and the solvent parameters. Correlations that are
frequently used are

$$\log k = a + bE_T(30) \qquad \text{and}$$
$$\log k = a + bE_T^N \qquad (4)$$

For numerous reactions, these correlations adequately express the dependence of the rate constant on the acidity parameter of the solvent [9-12]. As pointed out by Reichardt, the $E_T(30)$ values of protolytic solvents (and hence the E_T^N values too) reflect the participation as donor in hydrogen-bonding, and thus the electrophilicity. Our earlier investigations demonstrated that the amine exchange of Schiff bases is influenced considerably by the ability of the solvent to form hydrogen-bonds. We therefore studied the correlation between the rate constants for reactions 1-4 in the various solvent mixtures and the corresponding E_T^N values in accordance with (4). The constants a and b calculated with the method of least squares are to be found in Table II.

Table II

Application of regression equation (4) to reactions 1-4 in various solvent mixtures

Reaction No.	Solvent mixture	a	b	n	r
1	ethanol-n-hexane	-1.905	7.027	8[*]	0.965
2		-2.072	7.067	12[*]	0.939
3		0.157	2.485	7[*]	0.875
4		0.155	2.300	11[*]	0.872
1	ethanol-cyclohexane	-2.209	7.728	13	0.990
2		-2.279	7.537	12	0.992
3		0.655	·1.685	12[*]	0.918
4		0.480	1.806	12[*]	0.909
1	ethanol-benzene	-1.781	6.763	12	0.996
2		-2.157	7.000	12	0.999
3		-1.756	5.396	12	0.991
4		-2.092	5.774	12	0.994

[*]data (log k, E_T^N) relating to the pure apolar solvent were not used in the calculations

The data in Table II reveal that the values of $\underline{a}$ and $\underline{b}$ are affected appreciably by the nature of the Schiff base. For example, the data for reactions 1 and 2 barely differ in the solvent mixtures employed (of similar type), but they differ considerably from the data for reactions 3 and 4. The correlation coefficients point to a relatively close correlation between log k and E_T^N. However, the log k values calculated in accordance with (4) with the $\underline{a}$ and $\underline{b}$ data in Table II frequently differ significantly from the measured data. This is illustrated in Figs 1 and 2.
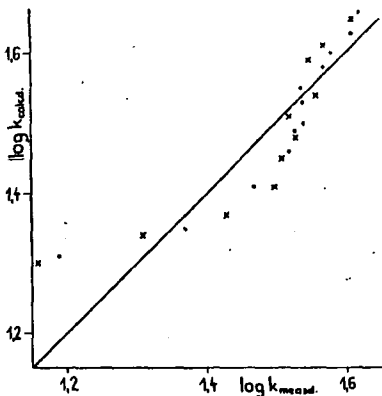

Fig. 1. Differences between the experimentally measured log k values for reaction 4 in ethanol-hexane (x) and ethanol-cyclohexane (•) mixtures and the values calculated via Eq. (4) with the data of Table II.
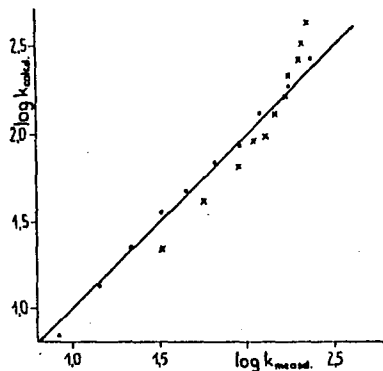
Fig. 2. Differences between the experimentally measured log k values for reaction 2 in ethanol-cyclohexane (x) and ethanol-benzene (•) mixtures and the values calculated via Eq. (4) with the data of Table II.

The differences between certain of the calculated and measured log k values are particularly large for reactions 3 and 4 in ethanol-n-hexane and in ethanol-cyclohexane mixtures. These differences, which are primarily to be observed in mixtures with low ethanol concentrations, indicate that it is not sufficient merely to take into account the acidity of the solvent for these systems; it is to be expected, for

instance, that the rate of the reaction is also influenced appreciably by the basicity of the solvent.

The use of a multiparameter equation to describe the solvent effect was introduced by Katritzky et al. [14]. In more recent investigations, a number of variations have been employed, in which use is made of the acidity and basicity parameters of the solvents, the molar refraction, the relative permittivity, the polarizability, the polarizing power, etc. A good review of the results to date is given by Svoboda et al. [15].

We have applied the following equation to describe the solvent effect observed in the amine exchange:

$$\log k = a + b_1 E_T^N + b_2 B_{KT} \tag{5}$$

where E_T^N and B_{KT} are the acidity and basicity parameters of the given solvent mixture, while $\underline{a}$, $\underline{b_1}$ and $\underline{b_2}$ are constants characteristic of the system. A correlation of this type was effectively utilized by Krygowski and Fawcett [16-18] to characterize the solvent effect quantitatively in various processes. The experimental data [1, 2, 4] were employed with the method of least squares to determine the constants or (5) for reactions 1-4, and the corresponding multiple correlation coefficient (R) was calculated. In order to be able to compare the effects of the acidity and the basicity, we also converted the regression coefficients b_1 and b_2 to beta coefficients β_1 and β_2, through the following equations [19, 17]:

$$\beta_1 = |b_1| \left(\frac{\sum_{i=1}^{n} (E_{T_{(i)}}^N - \overline{E_T^N})^2}{\sum_{i=1}^{n} (\log k_i - \overline{\log k})^2} \right)^{1/2} \quad , \quad \beta_2 = |b_2| \left(\frac{\sum_{i=1}^{n} (B_{KT_{(i)}} - \overline{B}_{KT})^2}{\sum_{i=1}^{n} (\log k_i - \overline{\log k})^2} \right)^{1/2} \tag{6}$$

where $\underline{i}$ denotes the data measured in the given solvent, while $\overline{E_T^N}$, $\overline{B_{KT}}$ and $\overline{\log k}$ are average values for the $\underline{n}$ experimental points. For the reactions in question, the distribution of the effects of the acidity and the basicity characteristic of the solvent was obtained as a percentage through the normalization of β_1 and β_2 [17]:

$$\beta_1' = \frac{100\ \beta_1}{\beta_1 + \beta_2} \qquad\qquad \beta_2' = \frac{100\ \beta_2}{\beta_1 + \beta_2} \qquad\qquad (7)$$
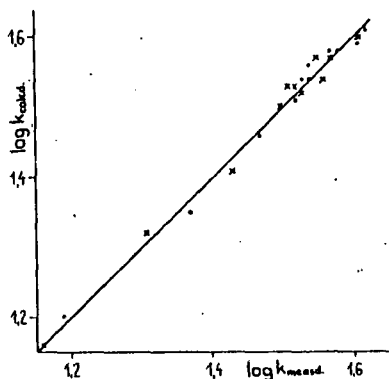

Fig. 3. Differences between the experimentally measured log k values for reaction 4 in ethanol-hexane (x) and ethanol-cyclohexane (•) mixtures and the values calculated via Eq. (5) with the data of Table III.
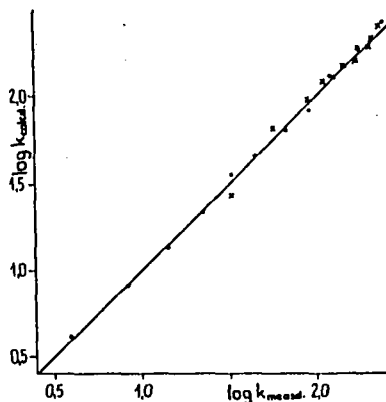
Fig. 4. Differences between the experimentally measured log k values for reaction 2 in ethanol-cyclohexane (x) and ethanol-benzene (•) mixtures and the values calculated via Eq. (5) with the data of Table III.

Figures 3 and 4 depict the measured log k values for some reactions, together with the calculated values obtained from the appropriate $\underline{a}$, $\underline{b_1}$ and $\underline{b_2}$ data in Table III.
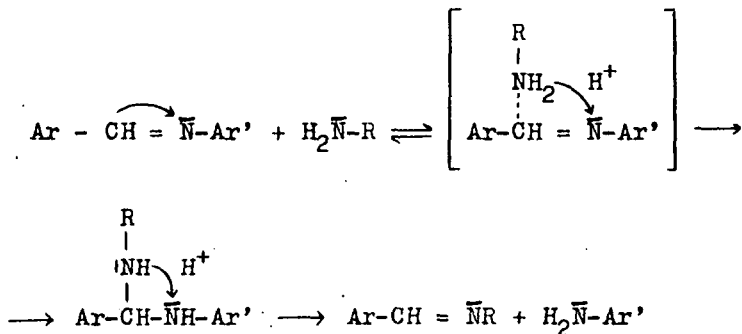
Table III

Application of regression equation (5) to reactions 1-4 in various solvent mixtures

Reaction No.	Solvent mixtures	a	b_1	b_2	β_1'	β_2'	n	R
1	ethanol-n-hexane	-2.196	6.371	0.855	76.70	23.30	8*	0.997
2		-2.614	6.515	1.065	71.90	28.10	12*	0.995
3		0.035	1.887	0.586	56.26	43.74	7*	0.994
4		-0.121	2.026	0.539	76.61	23.39	11*	0.995
1	ethanol-cyclohexane	-2.129	5.809	1.273	73.62	26.38	13	0.995
2		-2.227	5.186	1.598	67.20	32.80	12	0.999
3		0.501	1.284	0.477	61.58	38.42	12*	0.992
4		0.305	1.350	0.542	59.69	40.31	12*	0.993
1	ethanol-benzene	-1.978	8.201	-0.954	84.55	15.45	12	0.998
2		-2.300	8.037	-0.687	88.16	11.84	12	0.999
3		-2.065	7.645	-1.491	76.54	23.46	12	0.998
4		-2.347	7.628	-1.229	79.90	20.20	12	0.999

*data (log k, E_T^N) relating to the pure apolar solvent were not used in the calculations

From a comparison of Figs 1-4 and Tables II and III, it may be stated that Eq. (5) gives a good description (essentially better than Eq. (4)) of the solvent effect observed in these reactions. The rate of amine exchange of the Schiff bases is therefore influenced by both the acidity and the basicity of the solvent applied.

This result confirms the previously assumed reaction mechanism [20], and makes it more exact. If the solvent effect too is taken into consideration, the main steps are expected to be as follows:

$$Ar - \overset{\frown}{CH = N}-Ar' + H_2\bar{N}-R \rightleftharpoons \left[Ar-CH = \overset{\overset{\textstyle R}{|}}{\underset{\textstyle NH_2 \searrow H^+}{N}}-Ar' \right] \longrightarrow$$

$$\longrightarrow \overset{\overset{\textstyle R}{|}}{\underset{\textstyle |NH \searrow H^+}{Ar-CH-\bar{N}H-Ar'}} \longrightarrow Ar-CH = \bar{N}R + H_2\bar{N}-Ar'$$

This mechanism is in accord with the experience that the amine exchange takes place with appreciable rate only in solvents capable of hydrogen-bonding both as donors and as acceptors. The hydrogen-bonds developing●with the Schiff base and with the primary amine increase the electrophilic nature of the azomethine carbon atom, and also allow the proton transfers to occur through mediation of the solvent. Clearly, both effects increase the reaction rate.

The data in Table III reveal that, in all three solvent mixtures, the effect of the acidity is more significant than that of the basicity. It is also noteworthy that both b_1 and b_2 are positive in the ethanol-hexane and ethanol-cyclohexane mixtures, whereas in the ethanol-benzene mixtures b_2 is negative. In our opinion, this does not mean

that the basicity increases the reaction rate in the
ethanol-cyclohexane mixtures, for instance, and decreases
it in the ethanol-benzene mixtures. The negative sign may
arise as a computational result in consequence of the in-
teraction between the ethanol and benzene molecules, or
of the composition-dependent changes in the mixture. This
fits in with our earlier finding that the E_T^N values, and
particularly the B_{KT} values, vary in appreciably different
ways as functions of the mixture composition in ethanol-
-cyclohexane and ethanol-benzene mixtures [4].

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ИССЛЕДОВАНИЕ ВЛИЯНИЯ РАСТВОРИТЕЛЯ ПРИ АМИНООБМЕНЕ ОСНОВАНИЙ ШИФФА, V.

Связь коэфициента скорости с параметрами E_T^N и B_{KT} применяемых растворителей

П. Надь и Р. Херцфельд

Нами был исследован аминообмен оснований Шиффа в различных растворителях. По одному регрессивному уравнению установлена хорошая корреляция между коэфициентом скорости и параметрами E_T^N и B растворителей.