DETERMINATION OF LEWIS ACIDITY AND BASICITY PARAMETERS (E_T^N AND B_{KT}) IN ETHANOL-CYCLOHEXANE AND ETHANOL-BENZENE MIXTURES

By

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The E_T^N and B_{KT} values determined in ethanol-cyclohexane mixtures, and the E_T^N values determined in ethanol-benzene mixtures, demonstrate a simple correlation with the activity coefficient of ethanol.

Introduction

Since the classical investigations by MENSCHUTKIN [1], a huge number of experimental data have demonstrated that the rates of reactions taking place in the liquid phase, and also the position of the equilibrium, are frequently influenced considerably by the solvent applied [2]. "The rates of reactions in solution are often governed by the solvent, rather than by the chemical nature of the reaction partners." [3]. Nevertheless, in spite of the importance of this question and the extensive investigations that have been performed, there is still no general quantitative description of the solvent effect. The primary cause of this is that no exact and utilizable information is available concerning the internal structure of liquids. The interpretation of the solvent effect through the physical constants of the solvents (e.g. the relative permittivity [4]) is of only restricted use, for particular reaction types. If the large variety of intermolecular interactions is considered, however, a simple correlation of general validity is not to be expected. Accordingly, empirical parameters characteristic of the solvents have recently become widespread; if these are used appropriately, it is generally possible to give a good approximation to the magnitude of the solvent effect influencing the reaction rate or the chemical equilibrium.

The best-know of these parameters are the Y scale of GRUNWALD and WINSTEIN [5], the Z scale of KOSOWER [6] and the $E_T(30)$ scale of DIMROTH—REICHARDT [7]. The most widespread of these is the DIMROTH—REICHARDT acidity parameter, the value of which is known for more than 200 solvents [8] and numerous solvent mixtures [9—11], and the applicability of which has been tested widely [12].

The basicity parameters [13—16] are less well-known and less used. The reason for this is that the parameters introduced earlier are not sufficiently exact and their determination is limited. However, the basicity parameter described by KAMLET

and TAFT [17] (B_{KT}) is easy to measure and can be applied well; it has been slightly modified by KRYGOWSKI ET AL. [18].

We earlier reported that the rates of amine exchange in certain types of Schiff bases are appreciably influenced by the solvent used. We measured the rate constants of amine exchange for some reactions in ethanol-cyclohexane and ethanol-benzene mixtures [19—21]. We subsequently set out to establish what connection there is between the measured rate constants and the acidity and basicity parameters of the solvent mixtures used. We have therefore determined E_T^N and B_{KT} values for ethanol-cyclohexane and ethanol-benzene mixtures, for which experimental data have not previously been published.

Experimental

The 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio) phenolate necessary for deter-mination of the $E_T(30)$ values was kindly provided by Professor Reichardt (Marburg). This dye is strongly solvatochromic; its long-wave absorbance band is shifted con-siderably towards shorter wavelengths in solvents of higher polarity. If the position of the band maximum (λ, nm) is determined, the $E_T(30)$ value [7] is

$$E_T(30) = \frac{2.859 \cdot 10^4}{\lambda} \text{ kcal} = \frac{1.197 \cdot 10^5}{\lambda} \text{ kJ.} \qquad (1)$$

By normalization of the $E_T(30)$ values, the more practically useful dimensionless E_T^N data can be obtained [8], which in the solvent in question are

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

where $E_T(\text{water})$ and $E_T(\text{TMS})$ are the $E_T(30)$ values measured in water and tetra-methylsilane, respectively. Thus, the two end-points of the scale are water ($E_T^N = 1$) and TMS ($E_T^N = 0$). Since $E_T^N(\text{water}) = 63.1$ kcal and $E_T(\text{TMS}) = 30.7$ kcal [7], we have

$$E_T^N = \frac{E_T(\text{solvent}) - 30.7}{32.4}. \qquad (3)$$

To characterize the basicity of the solvent mixtures, we determined the modi-fied KAMLET—TAFT parameter. For this, the positions of the maximum for the long-wave absorbance bands of p-nitroaniline (pNA) and N,N-diethyl-p-nitroaniline (DEpNA) were measured in the given solvent mixtures. The following regression equation was used for calculation of the B_{KT} values [18]:

$$v_{\text{max}}^*(\text{pNA}) = 1.128 \quad v_{\text{max}}^*(\text{DEpNA}) + 0.319 \text{ kK.} \qquad (4)$$

This correlation applies to apolar, weak σ or π donor solvents (e.g. n-hexane, tetra-chloromethane, 1,2-dichloroethane), which are not able to form hydrogen-bonds either as an acceptor or as a donor. It must further be taken into consideration that DEpNA can take part in hydrogen-bond formation only as a hydrogen-acceptor, whereas pNA can do so both as an acceptor and as a donor. Thus, if the $v_{\text{max}}^*(\text{DEpNA})$

values measured in the various solvent mixtures are substituted into Eq. (4), data for v_{max}^*(pNA) can be calculated from which the effect of the basicity of the solvent has been eliminated. The measured v_{max}^*(pNA), however, is influenced both by the acidity and by the basicity, and hence the difference (Δv^*) between the measured and calculated values of v_{max}^*(pNA) will be characteristic of the basicity of the solvent. The basicity parameter B_{KT} was calculated via the following correlation [18]:

$$B_{KT} = \frac{\Delta v^*}{2.78} \tag{5}$$

where 2.78 kK is the Δv^* value for hexamethylphosphortriamide. Thus, the B_{KT} scale too is normalized; the most basic solvent is hexamethylphosphortriamide ($B_{KT}=1$), while the least basic ones ($B_{KT}=0$) are those for which Eq. (4) holds.

The v_{max}^* values were determined with a VSU 2P spectrophotometer. The solvents, which had purities corresponding to spectroscopic needs, were carefully freed from water.

Results and Discussion

The acidity and basicity parameters calculated with Eqs. (1) and (3) and with Eqs. (4) and (5), respectively, are listed in Table I.

The variation of the parameters as functions of the mole fraction (x_1) of ethanol is illustrated in Figs. 1 and 2. It may be seen that both parameters vary monotonously with x_1 in ethanol-benzene, while E_T^N also does so in ethanol-cyclohexane; however, in each case there is a very considerable deviation from linearity. The

Table I

E_T^N and B_{KT} parameters for ethanol-cyclohexane and ethanol-benzene mixtures at 25 °C

Ethanol mol/dm³	Ethanol-cyclohexane		Ethanol-benzene	
	E_T^N**	B_{KT}***	E_T^N**	B_{KT}***
0.000	0.077*	0.00*	0.127*	0.08
0.086	0.405	0.13	0.164	
0.171	0.431	0.26	0.260	0.13
0.428	0.460	0.51	0.344	0.18
0.856	0.480	0.73	0.381	0.22
1.713	0.517	0.85	0.428	0.34
3.425	0.542	0.87	0.470	0.50
5.138	0.562	0.87	0.501	0.56
6.850	0.567	0.87	0.531	0.61
8.563	0.582	0.86	0.548	0.64
10.276	0.595	0.84	0.569	0.69
11.988	0.611	0.83	0.584	0.70
13.701	0.623	0.80	0.611	0.73
15.413	0.635	0.79	0.633	0.77
17.126	0.651	0.78	0.655	0.78

* Literature data [8], [18].
** error in our E_T^N measurements less than ±0.005,
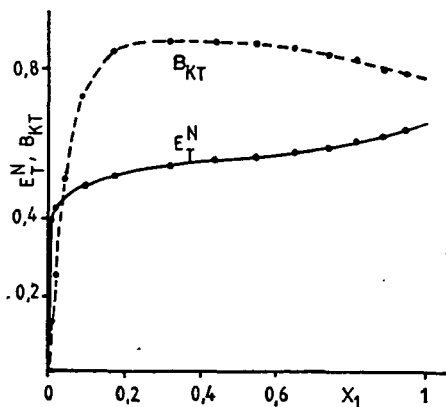*** measurement error less than ±0.03.

Fig. 1. Variation of E_T^N and B_{KT} values for ethanol-cyclohexane mixtures as a function of x_1
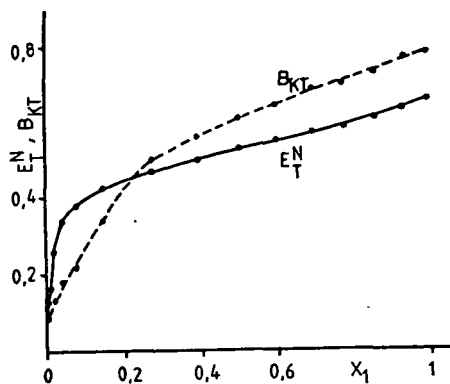
Fig. 2. Variation of E_T^N and B_{KT} values for ethanol-benzene mixtures as a function of x_1

B_{KT} values for ethanol-cyclohexane pass through a maximum. At low x_1 values, both parameters (but particularly E_T^N) increase steeply, while at higher x_1 values the curves flatten out.

At least two phenomena must be taken into consideration in connection with the interpretation of the shapes of the curves. One factor is that, when the solvent components are mixed, their original structures are broken down to various extents. This is important in the case of ethanol; the higher the mole fraction of the apolar component in the mixture, the lower the extent of association of the ethanol molecules. At low x_1, essentially free alcohol molecules are present, and thus both the acidity and the basicity of these can be well displayed. This is reflected in Figs. 3 and 4, where E_T^N/x_1 and B_{KT}/x_1 are plotted as functions of x_1. It can be seen that these "specific" data increase very quickly with the decrease of x_1.
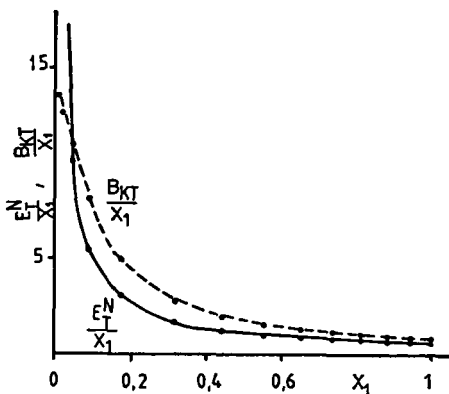

Fig. 3. Variation of E_T^N/x_1 and B_{KT}/x_1 values for ethanol-cyclohexane mixtures as a function of x_1
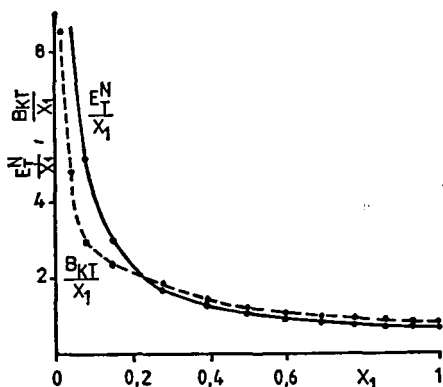
Fig. 4. Variation of E_T^N/x_1 and B_{KT}/x_1 values for ethanol-benzene mixtures as a function of x_1

The other factor is the interaction of the components of the mixture, in which significant roles are played by the acidities and basicities of the components [22]. Benzene and cyclohexane, for instance, have higher acidity than basicity; in mixtures with low x_1, therefore, the apolar component more effectively blocks manifestation of the basicity of ethanol. Figures 1 and 2 are in agreement with this, where the B_{KT} vs. x_1 curve falls more steeply than the E_T^N vs. x_1 curve towards $x_1=0$. In mixtures with higher x_1, this interaction is naturally no longer of significance.

From Figs. 1—4 it can be expected that the correlation between E_T^N, B_{KT} and the composition of the solvent mixture can not be described by a simple two-parameter equation. Accordingly, the equation introduced by LANGHALS [11] can not be applied to these systems. The same was observed by KRYGOWSKI ET AL. [22] for solvent mixtures containing methanol.
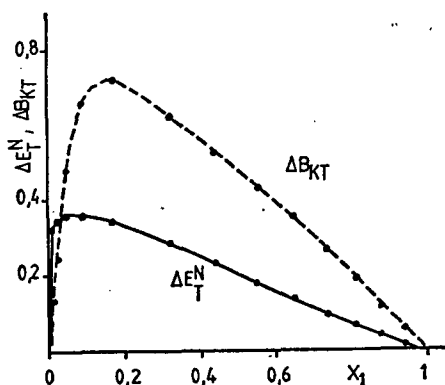

Fig. 5. Variation of ΔE_T^N and ΔB_{KT} values for ethanol-cyclohexane mixtures as a function of x_1

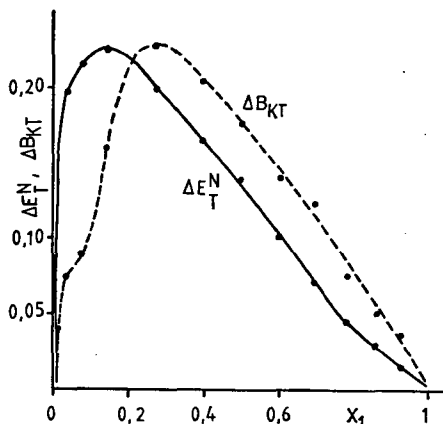Fig. 6. Variation of ΔE_T^N and ΔB_{KT} values for ethanol-benzene mixtures as a function of x_1

Figures 5 and 6 depict the differences of the E_T^N and B_{KT} values from additivity as functions of x_1. The differences, ΔE_T^N and ΔB_{KT}, were calculated via the known correlations

$$E_T^N - x_1(E_T^N)_1^* - x_2(E_T^N)_2^* = \Delta E_T^N$$

$$B_{KT} - x_1(B_{KT})_1^* - x_2(B_{KT})_2^* = \Delta B_{KT}$$

(6)

where the index 1 refers to ethanol, and the index 2 to cyclohexane or benzene. The difference from additivity (which stems from the effects of the interaction of the components of the mixture on the phenomenon in question) is seen to be greates in the mixtures with low x_1. Figures 3—6 and our earlier results relating to the solvent effect [20] led us to assume that the ΔE_T^N and ΔB_{KT} values determined for the given mixtures are connected with the activity coefficient of ethanol. To express this connection, we made use of an empirical correlation of the type

$$Y = x_1 Y_1^* + x_2 Y_2^* + x_1 x_2 B$$

(7)

which can frequently be applied well to describe the properties of two-component mixtures. In this case, Y denotes the corresponding E_T^N or B_{KT} value, in accordance with Eq. (6), while B denotes the difference from additivity. Figures 7 and 8 depict the B values calculated from the data in Table I, as functions of the activity coefficient of ethanol [23, 24]. It is clear that, to a very good approximation, the data relating to both the acidity and the basicity for the ethanol-cyclohexane mixtures vary linearly with the activity coefficient of ethanol. The regression equations for the straight lines are

$$B = \Delta E_T^N / x_1 x_2 = -0.148 + 0.556\,\gamma_1, \quad n = 10, \quad r = 0.9994 \tag{8}$$

$$B = \Delta B_{KT} / x_1 x_2 = 0.264 + 0.979\,\gamma_1, \quad n = 11, \quad r = 0.9992, \tag{9}$$

The correlation between B and γ_1 is seen to be very good.
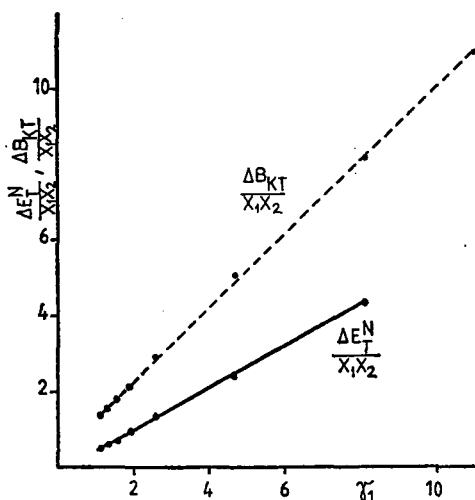

Fig. 7. Variation of $B(\Delta E_T^N/x_1 x_2$ and $\Delta B_{KT}/x_1 x_2)$ for ethanol-cyclohexane mixtures as a function of γ_1, the activity coefficient of ethanol
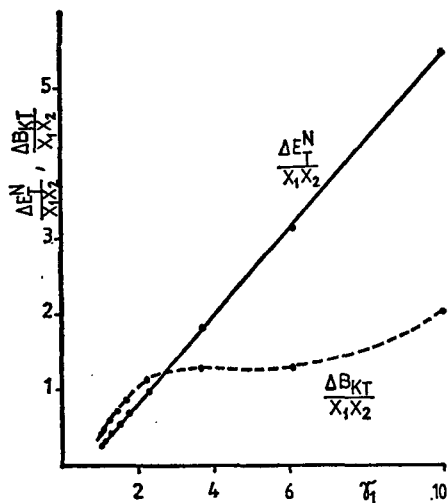
Fig. 8. Variation of $B(\Delta E_T^N/x_1 x_2$ and $\Delta B_{KT}/x_1 x_2)$ for ethanol-benzene mixtures as a function of γ_1

For the ethanol-benzene mixtures, the linearity and correlation are similarly good for the acidity:

$$B = \Delta E_T^N / x_1 x_2 = -0.320 + 0.578\,\gamma_1, \quad n = 11, \quad r = 0.9998. \tag{10}$$

However, the data relating to the basicity do not vary linearly with γ_1.

The reported results demonstrate that both the acidity and the basicity parameter for ethanol-cyclohexane mixtures, and the acidity parameter for ethanol-benzene mixtures, vary in parallel with the composition of the mixture and with the activity coefficient of ethanol, in accordance with Eqs. (7)—(10). This is presumably a consequence of the variations in the acidity and basicity parameters and the activity coefficient being determined by the structure of the liquid, and

predominantly by the association of the alcohol molecules. The latter depends considerably on the composition of the mixture, i.e. on the relative content of the apolar component. It is probable that, additionally, the effect of the apolar component on the parameters in question corresponds to the additivity. The basicity parameter for the ethanol-benzene mixtures varies in a different manner with the composition of the mixture. This is presumably caused by the π donor nature of the benzene molecule, or by the composition-dependent difference from additivity influencing the B_{KT} values.

Finally, it should be noted that, when the solvent effect was studied in the amine exchange of Schiff bases [20], the variations of $\log k$ measured in ethanol-cyclohexane and ethanol-benzene mixtures could similarly be described by means of a correlation corresponding to Eqs. (7) and (8). Thus, it is to be expected that the rate constant is directly correlated with the acidity and basicity parameters, which is in accordance with the assumed mechanism of amine exchange. This problem will be dealt with in our next paper.

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ОПРЕДЕЛЕНИЕ ПАРАМЕТРОВ КИСЛОТНОСТИ И ОСНОВНОСТИ ПО ЛЮИСУ (E_T^N, B_{KT}) В БИНАРНЫХ РАСТВОРАХ ЭТАНОЛ-ЦИКЛОГЕКСАН И ЭТАНОЛ-БЕНЗОЛ

П. Надь и Р. Герцфельд

Показано, что значения E_T^N и B_{KT}, определенные в этанольно-циклогексановом растворе, а такие E_T^N в этанольно-бензольном растворе находятся в простой зависимости от коэффициента активности этанола.