

Studies in Organic Chemistry 42

# **SIMILARITY MODELS IN ORGANIC CHEMISTRY, BIOCHEMISTRY AND RELATED FIELDS**

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**ELSEVIER**

Amsterdam — Oxford — New York — Tokyo 1991

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CHAPTER 6

DESCRIPTION OF PROPERTIES OF BINARY SOLVENT MIXTURES

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## 1. INTRODUCTION

Similarity models can be used for predictions on the basis of only few experimental data and are important for the the investigation of solvent effects. The polar properties of media play a key part in chemical and biochemical reactions. The effect of solvents on chemical reactions may be as high as several powers of ten in reaction rate and the choice of the solvent may completely control the formation of reaction products; for a review see (1-2).

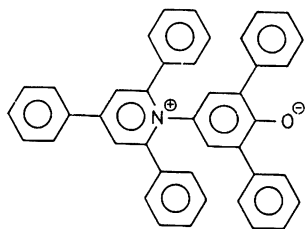
This has stimulated the development of empirical polarity scales and two well-known polarity scales are given here as examples: see (1). The Winstein Y scale (3), defined in equation 1:

$$Y = \lg (k/k_0) \quad [1]$$

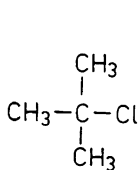
$$E_T(30) = 28590 [\text{kcal} \cdot \text{mol}^{-1}] / \lambda_{\text{max}} \quad [2]$$

has as a basis the rate constant  $k$  of a chemical reaction; namely, the solvolysis of tert-butyl chloride, with the reference solvent 80% ethanol/water ( $k_0$ ). On the other hand, the  $E_T(30)$  scale of Dimroth and Reichardt (4-7), the definition of which is given in equation 2, is derived from a spectroscopic effect: the solvatochromism (the peak shift  $\lambda_{\text{max}}$  in the uv/vis absorption) of dye I.  $E_T(30)$  is the molar energy of excitation of the dye in the corresponding solvent.

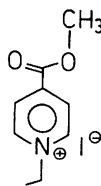
The empirical polarity scales are well established for pure organic solvents and are important tools for mechanistic- and preparative-oriented chemists. However, hardly any chemical reactions are carried out in pure liquid phases. Normally a starting material is dissolved in a solvent to run a chemical reaction, and thus the reaction mixture even at the beginning is binary or has even more components. During the reaction the products can be considered as further components, and, as well as this, the solvents are usually of technical grade and contain other substances as impurities, the most common and important of these being water. This is obvious when a sensitive polarity scale, e.g. the  $E_T(30)$  scale, is used to the determine the polarity of a solvent sample.



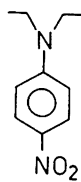
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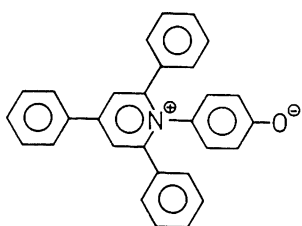
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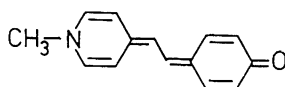
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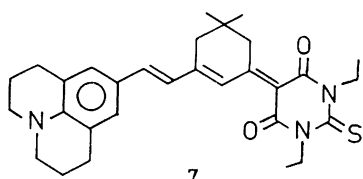
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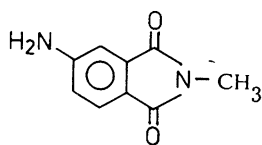
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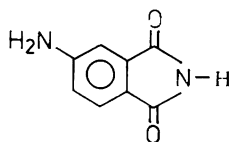
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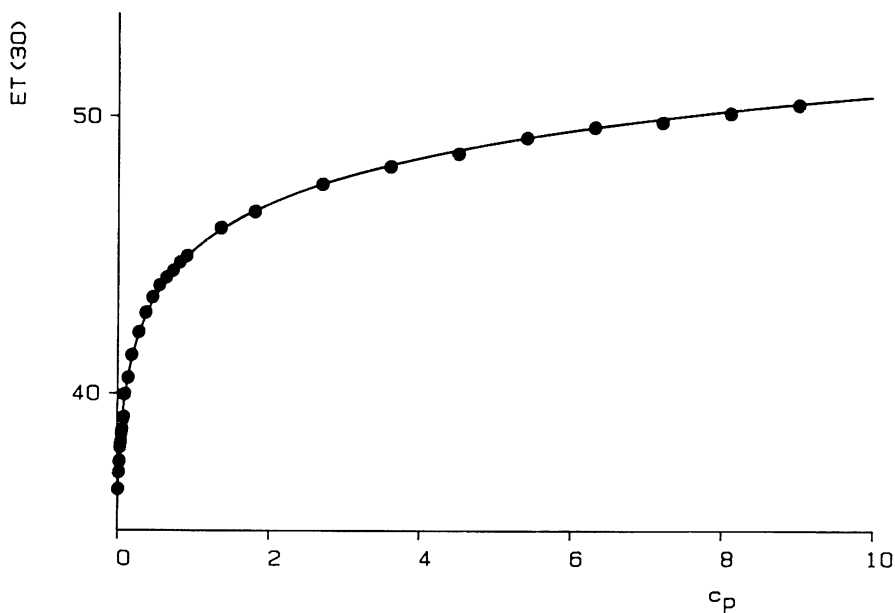
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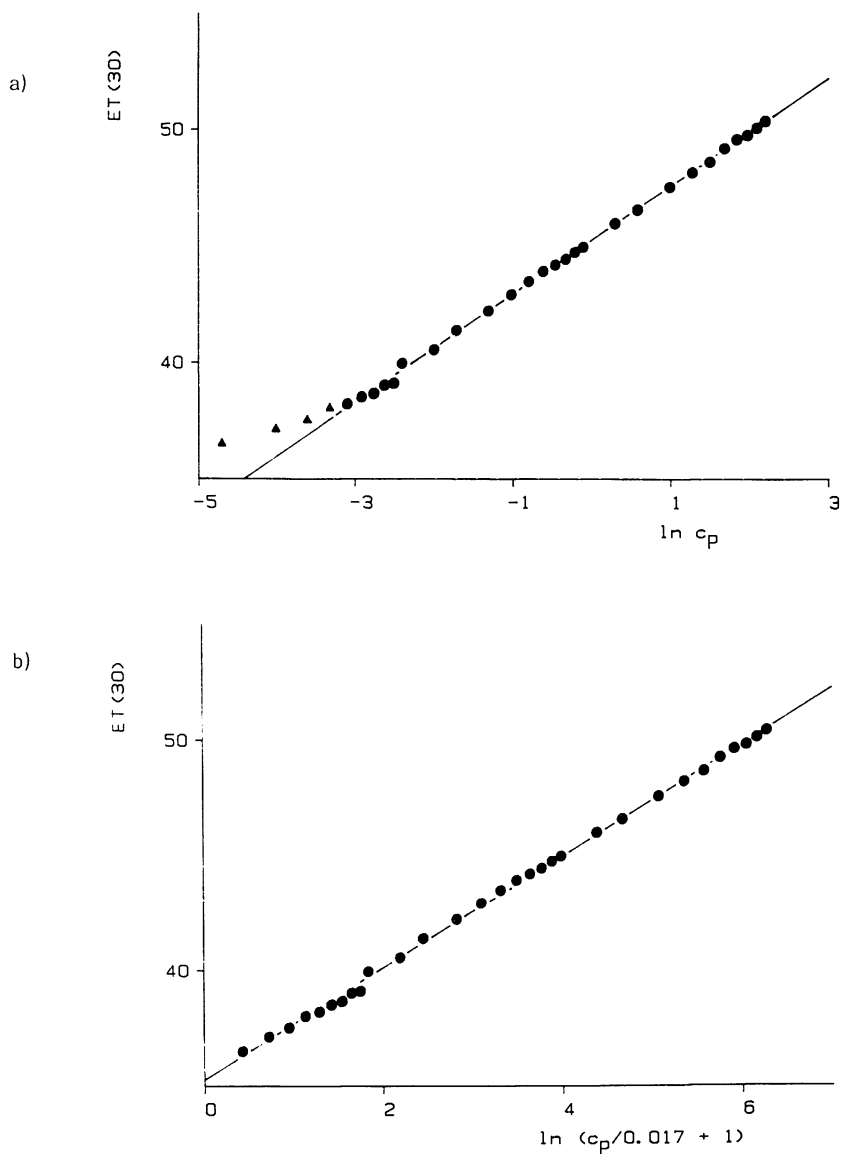
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## 2. BINARY LIQUID MIXTURES

The necessity to develop a quantitative relation between the composition and the polarity of a binary mixture seems thus to be obvious. Empirical polarity scales are well established for pure solvents - so the next aim should be their extension to binary mixtures. However, judging by the literature, this has proved to be a serious problem. For pure solvents (1) generally useful linear correlations are obtained between different polarity scales, for example between the Winstein Y scale and the  $E_T(30)$  scale already mentioned. Surprisingly, however, the linear correlation which applies to pure solvents deteriorates when solvent mixtures are included (1,8,9). Moreover the polarities of mixtures measured as a function of their composition in vol % or mole % give complex curves (4,8,10), in some cases even with maxima and minima (11,12).



**Fig.1:** Plot of the  $E_T(30)$  values against  $c_p$  for the binary mixture N-tert-butylformamide/benzene.



**Fig.2:** a) Plot of the  $E_T(30)$  values against  $\ln c_p$  for the binary mixture N-tert-butylformamide/benzene - b) plot of  $E_T(30)$  against  $\ln (c_p / (c^* + 1))$  according to equation 3.

Several attempts have been made to find a general solution to this problem, see for example (13,14,15), a typical example of which is given by fig.1, where the  $E_T(30)$  values for the mixture N-tert-butylformamide/benzene are plotted against  $c_p$ , the molar concentration of the more polar component (N-tert-butylformamide).

But a solution of the problem first came about with the observation that a plot of the  $E_T(30)$  values against the logarithm of the molar concentration of the more polar component of a binary mixture gave a straight line at high concentrations (16,17) as shown in Fig. 2a.

At low concentrations the plot deviates from a straight line and as  $c_p \rightarrow 0$ , it tends to  $E_T(30)^0$ , the  $E_T(30)$  value of the less-polar component. For the whole concentration range the two-parameter equation 3 could be developed, with which the entire curve, including the curved section, can be described in closed form (16-17):

$$E_T(30) = E_D \ln (c_p/c^* + 1) + E_T(30)^0 \quad [3]$$

$E_T(30)$ ,  $E_T(30)^0$ , and  $c_p$  were defined above, and  $E_D$  and  $c^*$  are the parameters of the equation. These latter can be determined graphically (16) or by using a computer program which varies the parameter  $c^*$  and takes the correlation coefficient of the plot of  $E_T(30)$  against  $\ln (c_p/c^*+1)$  as a test for linearity.

The validity of equation 3 can be demonstrated by a plot of  $E_T(30)$  against  $\ln (c_p/c^*+1)$  which is given in fig. 2b for the data of fig. 1. The straight line which is shown covers a concentration range of three orders of magnitude. Deviations from the straight line are statistical in nature and correspond to experimental error.

### 3. THE PARAMETERS OF EQUATION 3

The parameter  $E_D$  has the dimensions of energy and is a measure of the sensitivity of the  $E_T(30)$  scale towards relative changes of  $c_p$ . The parameter  $c^*$  has the dimensions of concentration and is the concentration of the polar component above which the interaction between the two solvent components becomes important for the polarity of the mixture. Thus  $c^*$  divides the



concentration region into two parts. This is best illustrated by the limiting behaviour of function 3.

$$E_T(30) = E_D \ln (c_p/c^* + 1) + E_T(30)^0 \quad [3]$$

$$E_T(30) = \frac{E_D}{c^*} c_p + E_T(30)^0 \quad [4]$$

$$E_T(30) = E_D \cdot \ln c_p + (E_T(30)^0 - E_D \cdot \ln c^*) \quad [5]$$

For low concentrations of the polar component,  $c_p \ll c^*$ , one may obtain equation 4 by applying a Taylor type series expansion to equation 3. Thus in this concentration range, the contributions of both components to polarity are cumulative (see below).

For high concentration,  $c_p \gg c^*$ , the quotient  $c_p/c^*$  becomes large compared to 1, and equation 3 can be simplified to obtain equation 5. In this concentration region we have a linear dependence of  $E_T(30)$  on  $\ln c_p$ . This corresponds to the linear part in fig. 2a.

The experimentally accessible range of  $c_p$  extends from the pure, less-polar component,  $c_p = 0$ , to the pure, more-polar component,  $c_p = c_p^{\max}$ . If the parameter  $c^*$  of equation 3 for the mixture under test is large,  $c^* \gg c_p^{\max}$ , a linear relationship is obtained over the whole concentration region. In this case the frequently postulated linear relationship between the polarity and the composition of a mixtures, see reviews (1,9-10,12,18), is satisfied. If, however,  $c^*$  is small, say  $< 0.06$  mol/l, the correlation between polarity and  $c_p$  is non-linear over the

experimentally relevant concentration range. This is demonstrated in fig. 1 for the binary mixture N-tert-butylformamide/benzene, for which  $c^*$  is low.

There is still another important result from equation 3 due to the logarithmic relation between the concentration and the polarity of a binary mixture: the addition of a small amount of a polar solvent to a solvent with a low polarity will markedly increase the polarity of the medium. On the other hand, the addition of a little solvent with low polarity to a polar solvent will not result in a noticeable decrease in polarity. This corresponds to practical experience, for example, with chromatography or the effect of additives on reaction rates of chemical reactions. From equation 3 it is obvious that the magnitude of the effect increases with decreasing  $c^*$  values.

#### 4. FURTHER POLARITY SCALES

The experimental validity of equation 3 for the  $E_T(30)$  scale has also been found for other polarity scales (18-21) and can be expressed in general form by equation 6.

$$P = E_D \ln (c_p/c^* + 1) + P^0 \quad [6]$$

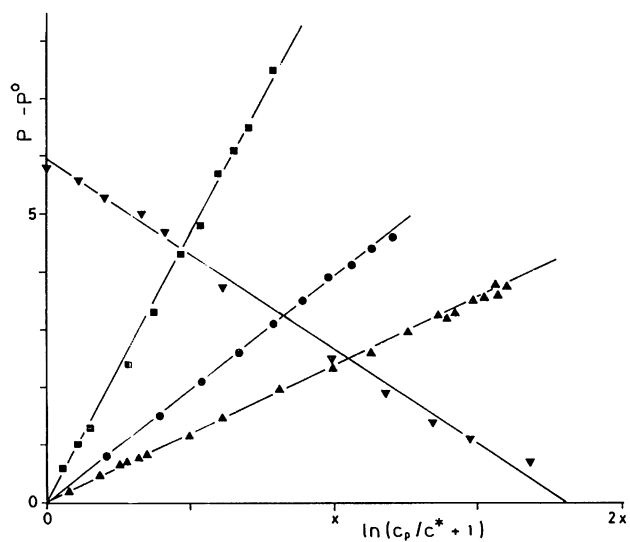
In equation 6  $P$  is the polarity of a binary mixture measured by an empirical polarity scale.  $P^0$  is the polarity of the pure, less polar component.  $E_D$ ,  $c^*$ , and  $c_p$  have the same meaning as in equation 3. Essentially both equations show similar limiting behaviour when extreme values are considered.

Empirical polarity scales, a selection of which is shown in Table 1, are based on various effects, such as  $\pi \rightarrow \pi^*$  absorption (Nos. 1,4-7), charge-transfer absorption (No. 3), fluorescence (Nos. 8,9) and solvolysis (No. 2). The  $E_T(1)$  scale (No. 5) responds not only to the polarity of the medium, but also shows sensitive response to its hydrogen-bonding donor character.

In terms of the criteria used in all polarity scales studied to date, equation 6 is a valid description of polar behaviour of binary liquid mixtures as a function of their composition (17,19). The linear relationship between  $P$  or  $P - P^0$ , respectively, and  $\ln (c_p/c^* + 1)$ , for some polarity scales mentioned in Table 1 is illustrated in figure 3.

**Table 1:** Empirical solvent polarity scales; see (1,17).

No.	polarity scale	solvent dependent probe	process
1	$E_T(30)$	<b>1</b>	$\pi \rightarrow \pi^*$ absorption
2	Y	<b>2</b>	solvolysis reaction
3	Z	<b>3</b>	CT-absorption
4	$\pi_1^*$	<b>4</b>	$\pi \rightarrow \pi^*$ absorption
5	$E_T(1)$	<b>5</b>	$\pi \rightarrow \pi^*$ absorption
6	MOED	<b>6</b>	$\pi \rightarrow \pi^*$ absorption
7	$\chi_R$	<b>7</b>	$\pi \rightarrow \pi^*$ absorption
8	$S_1$	<b>8</b> , R=CH <sub>3</sub>	fluorescence
9	$S_2$	<b>9</b> , R=H	fluorescence



**Fig.3:** Linear relationship between  $P$  and  $\ln(c_p/c^* + 1)$  for various polarity scales (equation 3):  $\blacktriangle$   $E_T(30)$  ethanol - 1-decanol,  $x = 1$ ;  $\bullet$  Y water-methanol,  $x = 2$ ;  $\blacksquare$  Z methanol-acetone,  $x = 2$ ;  $\blacktriangledown$   $\pi_1^*$  ethanol - n-heptane,  $x = 1$ , ordinate  $P - P^0 + 5.8$

**Table 2:** The parameters  $E_D$  and  $c^*$  from equation 6 for binary solvent mixtures and various solvent polarity scales G.

No.	components <sup>a)</sup>	$E_D$ kcal/mol	$c^*$ mol/l	$P_G^o$ kcal/mol G	r n	$c_k$ mol/l
1	butanol acetone	1.99	0.14	42.2 1	0.9995 31	
2	ethanol acetone	2.27	0.14	42.2 1	0.9994 28	
3	methanol acetone	2.53	0.10	42.2 1	0.9997 29	
4	N-tert-butylformamide acetone	1.87	0.27	46.0 1	0.9995 31	
5	water acetone	3.59	0.664	42.2 1	0.9994 11	6
	(water acetone <sup>b)</sup>	242	1000 <sup>c)</sup>	48.9 1	0.9956 9)	
6	ethanol acetonitrile	1.83	0.10	46.0 1	0.9997 30	
7	1-hexanol acetonitrile	1.08	0.08	46.0 1	0.9988 29	12
8	methanol acetonitrile	1.83	0.06	46.0 1	0.9988 31	
9	water acetonitrile	2.70	0.293	45.7 1	0.9992 11	6
	(water acetonitrile <sup>b)</sup>	132	1000 <sup>c)</sup>	53.3 1	0.9921 8)	
10	N-tert-butylformamide benzene	2.27	0.01	34.5 1	0.9985 31	

No.	components <sup>a)</sup>	E <sub>D</sub> kcal/mol	c* mol/l	P <sub>G</sub> <sup>o</sup> kcal/mol G	r n	c <sub>k</sub> mol/l
11	water	1.33	1.98	49.8	0.9981	
	1-butanol			1	22	
	(water 1-butanol <sup>b)</sup>	33.8	10 <sup>-4</sup>	-384	0.9901	6)
12	water tert-butyl- hydroperoxide	1.42	0.340	49.7	0.9984	
				1	10	
13	water tert-butyl alcohol	2.82	1.01	43.3	0.9967	
				1	26	
14	water N-tert-butyl- formamide	4.90	28.2	50.4	0.9965	
				1	21	
15	1-butanol carbon disulphide	2.42	0.03	32.6	0.9991	8
				1	30	
16	1-octanol carbon disulphide	2.83	0.06	32.6	0.9968	4
				1	30	
17	pinacolone carbon disulphide	9.30	7.89	32.6	0.9946	
				1	16	
18	water dimethoxyethane	3.00	0.301	38.2	0.9996	
				1	12	
19	water dimethylacetamide	5.19	5.28	43.0	0.9984	
				1	13	
20	water DMEU <sup>d,e)</sup>	9.49	11.0	42.5	0.9992	
				1	20	
21	1-butanol DMF	3.20	1.64	43.8	0.9994	8
				1	30	
22	ethanol DMF	2.78	0.607	43.8	0.9979	14
				1	30	

No.	components <sup>a)</sup>	$E_D$ kcal/mol	$c^*$ mol/l	$P_G^0$ kcal/mol G	$r_n$	$c_k$ mol/l
23	methanol DMF	3.55	0.696	43.8 1	0.9975 31	
24	water DMF	9.56	11.52	43.7 1	0.9979 18	39
25	1-butanol DMSO	4.93	4.29	43.8 1	0.9953 30	
26	ethanol DMSO	3.95	2.69	45.0 1	0.9979 30	14
27	water DMSO	24.0	53.8	45.1 1	0.9997 20	
28	acetonitrile 1,4-dioxan	3.23	0.77	36.0 1	0.9991 29	
29	1-butanol 1,4-dioxan	5.39	0.90	36.0 1	0.9997 30	
30	ethanol 1,4-dioxan	4.99	0.72	36.0 1	0.9998 30	
31	methanol 1,4-dioxan	4.55	0.35	36.0 1	0.9992 30	
32	nitromethane 1,4-dioxan	3.49	1.01	36.0 1	0.9993 31	
33	propionitrile 1,4-dioxan	3.33	1.41	36.0 1	0.9983 30	
34	water 1,4-dioxan (water 1,4-dioxan <sup>b)</sup>	4.33  368	0.512  1000 <sup>c)</sup>	36.0  43.8	0.9993  0.9969 8)	

No.	components <sup>a)</sup>	$E_D$ kcal/mol	$c^*$ mol/l	$P_G^o$ kcal/mol G	$r_n$	$c_k$ mol/l
35	water DMPU <sup>e,f)</sup>	10.5	12.8	42.1 1	0.9996 18	
36	water ethanol (water ethanol <sup>b)</sup>	6.29 14.3	38.1 $10^{-4}$	52.0 -126 1	0.9987 0.9980 9)	34
37	water formamide	5.58	34.3	55.9 1	0.9962 10	39
38	water HMPA <sup>g)</sup>	563	$1000^c)$	40.9 1	0.9989 6	
39	water methanol (water methanol <sup>b)</sup>	17.9 9.13	150 $10^{-4}$	55.4 -57.9 1	0.9300 0.9920 8)	37
40	water methoxyethanol (water methoxyethanol <sup>b)</sup>	1.80 271	12.4 $1000^c)$	52.2 48.4 1	0.9802 0.9982 6)	
41	water N-methylpyrrolidone	12.3	17.4	42.2 1	0.9996 18	
42	1-butanol nitromethane	1.43	0.06	46.3 1	0.9991 31	7
43	ethanol nitromethane	1.41	0.03	46.3 1	0.9970 30	9
44	methanol nitromethane	1.66	0.01	46.3 1	0.9995 29	10

No.	components <sup>a)</sup>	$E_D$ kcal/mol	$c^*$ mol/l	$P_G^o$ kcal/mol G	$r$ n	$c_k$ mol/l
45	water	4130	1000 <sup>c)</sup>	46.3	0.9997	
	nitromethane			1	3	
46	water	1.69	4.22	50.5	0.9956	
	1-propanol			1	25	
	(water	23.5	$10^{-4}$	-126	0.9952	
	1-propanol <sup>b)</sup>			1	11)	
47	water	3.09	0.502	46.0	0.9990	
	propylene carbonate			1	9	
48	acetone	4.01	32.1	40.2	0.9871	
	pyridine			1	28	
49	1-dodecanol	2.90	0.89	40.2	0.9990	3
	pyridine			1	30	
50	ethanol	9.64	12.8	40.2	0.9955	
	pyridine			1	31	
51	1-hexanol	2.90	1.11	40.2	0.9976	
	pyridine			1	30	
52	methanol	6.92	5.84	40.2	0.9981	
	pyridine			1	31	
53	nitromethane	6.46	13.6	40.2	0.9938	
	pyridine			1	30	
54	tert-pentyl alcohol	1.02	0.95	40.2	0.9934	
	pyridine			1	29	
55	water	7.09	5.48	40.2	0.9960	
	pyridine			1	29	



No.	components <sup>a)</sup>	E <sub>D</sub> kcal/mol	c* mol/l	P <sub>G</sub> <sup>o</sup> kcal/mol G	r n	c <sub>k</sub> mol/l
56	water	4.03	0.449	37.4	0.9997	
	tetrahydrofuran			<b>1</b>	20	
	(water tetrahydrofuran <sup>b)</sup>	302	1000 <sup>c)</sup>	45.1	0.9690	
				<b>1</b>	20)	
57	1-butanol TMU <sup>h)</sup>	3.56	0.91	41.0	0.9994	
				<b>1</b>	31	
58	ethanol TMU <sup>h)</sup>	3.51	0.81	41.0	0.9993	
				<b>1</b>	31	
59	water TMU <sup>h)</sup>	5.82	4.02	41.0	0.9986	
				<b>1</b>	14	
	(water TMU <sup>b,h)</sup>	300	1000 <sup>c)</sup>	45.9	0.9989	
				<b>1</b>	5)	
60	methanol acetone	2.25	0.31	49.3	0.9995	
				<b>6</b>	30	
61	water ethanol	2.04	5.47	55.9	0.9917	30
				<b>6</b>	24	
62	water ethanol	-1.71	3.08	72.9	-0.9985	30
				<b>4</b>	31	
63	ethanol n-heptane	-3.19	3.05	78.7	-0.9977	
				<b>4</b>	31	
64	ethanol acetonitrile	2.15	0.48	72.1	0.9987	7
				<b>3</b>	47	
65	methanol acetone	4.66	0.65	66.3	0.9999	
				<b>3</b>	31	

No.	components <sup>a)</sup>	$E_D$ kcal/mol	$c^*$ mol/l	$P_G^o$ kcal/mol G	$r$ n	$c_k$ mol/l
66	methanol	8.52	2.66	63.7	0.9938	
	1,4-dioxan			3	31	
67	water	6.67	49.7	35.2	0.9974	25
	ethanol			5	34	

a) The more polar component is mentioned first. - b) For high concentrations of polar component ( $c > c_k$ ). - c) More than 1000 mol/l. - d) 1,3-Dimethyl-2-imidazolidinone (70). e) Substitute for HMPA. f) 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone. - g) Caution (71,72) - highly toxic! - h) Tetramethylurea.

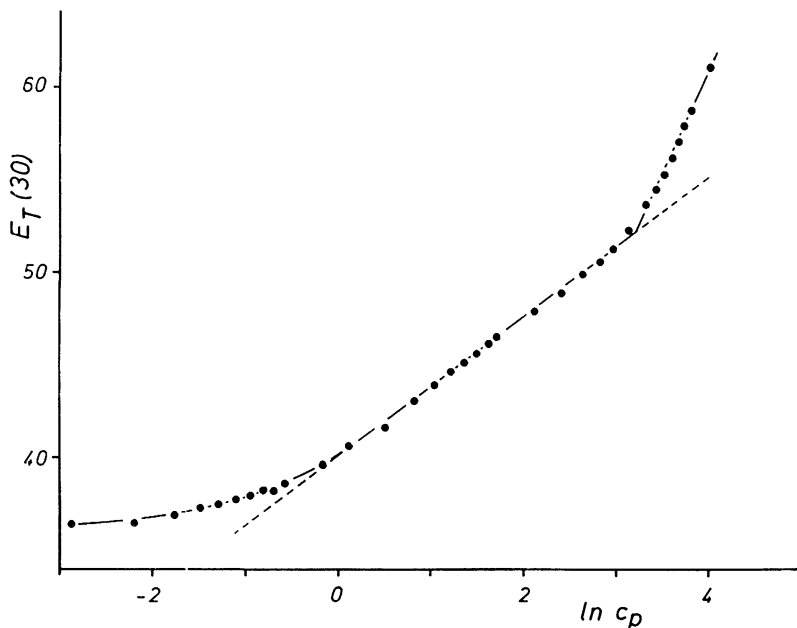
Table 2 gives an impression of the range of validity of equation 6, and shows the result of applying it to various polarity scales. The number and variety of the components used - polar protic, dipolar aprotic, and non-polar solvents, including aromatic solvents - lead to the conclusion that equation 6 provides a general description of the polarity of binary mixtures and is not confined to certain types (22) of solvent. Its validity for scale 5 and the mixture ethanol/water (19), which has a strong tendency to form hydrogen bonds, is particularly notable. Thus polarity effects caused by hydrogen bonding are also described by equation 6.

## 5. SPECIAL BINARY MIXTURES

Special features are observed with the solvent mixture water/1,4-dioxan. It was postulated in another context that 1,4-dioxan acts as a "solvent-structure-breaker" (23). This special property of the solvent can be investigated using equation 3.

Normal behaviour according to equation 3 is observed with the  $E_T(30)$  scale up to a water content of ca. 50%; this is seen in the left region of Fig.4. At a certain concentration  $c_k$ , however, the linear relationship abruptly gives way to a second steeper relationship with other  $E_D$  and  $c^*$  values (19).

In the following discussion, the concentration ranges  $c_p < c_k$  and  $c_p > c_k$  are designated region I and region II. For the mixture water/1,4-dioxan, the sudden change at  $c_k$  (discontinuity in the 1st derivative) can even be detected if  $E_T(30)$  is plotted against  $\ln c_p$ , i.e. without introducing further parameters.



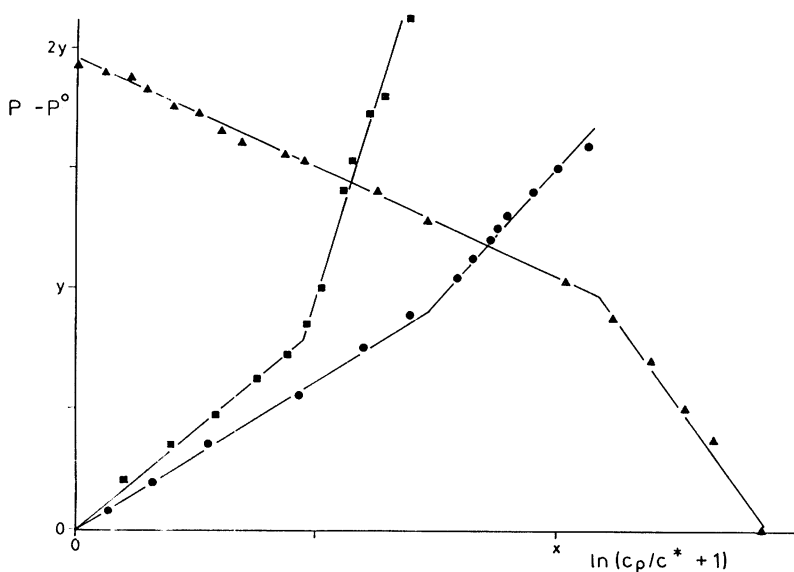
**Fig.4:** Double line for the mixture water/1,4-dioxan -  $E_T(30)$  versus  $\ln c_p$  according to equation 3 (see text).

The existence of two regions of validity for equation 3 with a critical change at  $c_k$  could be interpreted by assuming that in region I, at low water concentrations, the water molecules remain isolated and that the formation of a three-dimensional hydrogen bonded structure of water occurs in region II. This model is consistent with the postulated action of 1,4-dioxan as a "solvent-structure-breaker" (see above).

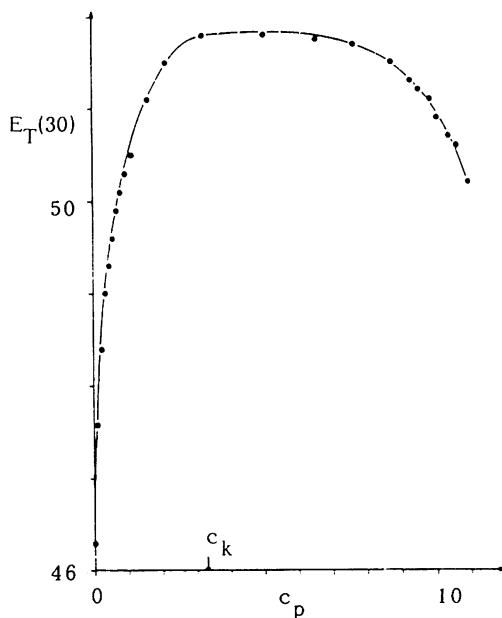
In Fig.4, the line of region I can be extrapolated into region II (broken line). Thus, for  $c_p = c_p^{\max}$ , a virtual polarity value is obtained for water  $E_T(30)_v = 56$ , which is smaller than the actual polarity value of 63.1 (6).  $E_T(30)_v$  is the polarity with

which water, as the more polar component, affects 1,4-dioxan within region I. Since the effective polarity of water is substantially lower at high dilution, than in concentrated solutions, one might venture to conclude that specific interaction of water molecules in molecular associates is responsible for the high polarity of pure water, rather than the characteristics of the isolated water molecule.

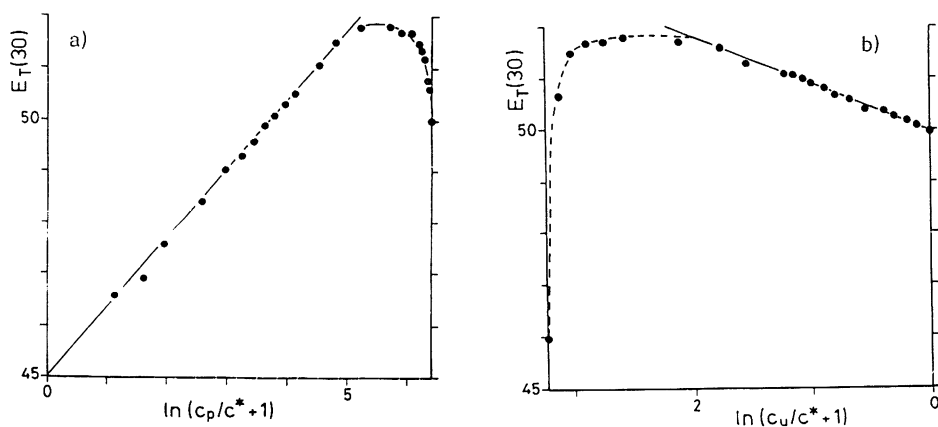
The occurrence of a second, steeper line according to equation 3 is not confined to the mixture water/1,4-dioxan, but can also be observed with other mixtures, especially with those including water, although the effect is not as pronounced as with water/1,4-dioxan. The mixture water/ethanol, which is very important for studies of reaction mechanisms, has been studied extensively using several polarity scales (19). All scales studied produced double straight lines (three examples are shown in Fig.5).



**Fig.5:** Double lines according to equation 6 for the mixture water/ethanol: ● Y,  $x = 2$ ,  $y = 1$ ; ■  $E_T(1)$ ,  $x = 1$ ,  $y = 4$ ; ▲  $\pi_1^*$ ,  $x = 1$ ,  $y = 4$ , ordinate:  $P - P^0 + 7.7$  ( $x$  and  $y$  are scaling factors for fig.5).



**Fig.6:**  $E_T(30)$  values of 1-butanol/nitromethane as a function of the molar concentration of 1-butanol.



**Fig.7:** a) Relationship between  $E_T(30)$  and  $\ln(c_p/c^* + 1)$ , b) relationship between  $E_T(30)$  and  $\ln(c_u/c^* + 1)$ . Both for the mixture 1-butanol/nitromethane.

It is remarkable that the various polarity scales produce  $c_k$  values which coincide within the limits of experimental error; in Fig.5 the break points appear at different abscissae since the  $c^*$  values vary for each polarity scale. Thus, the double line phenomenon is not peculiar to the  $E_T(30)$  scale, but must be taken as a characteristic of the binary mixture water/ethanol. The solvent polarity scale is only an indicator for the change in solvent structure. A further striking evidence for the change in solvent structure is the dependence of rate constant for the reaction between U(IV) and U(VI) (24) as a function of the composition of an ethanol/water mixture.

Even more interesting than the examples mentioned above are mixtures of 1-butanol and acetonitrile or nitromethane, and of ethanol and nitromethane, which represent a further type of binary mixture (21). Here the polarity of the mixture increases and reaches a maximum at  $c_k$ . As  $c_p$  increases further, however, the polarity again decreases and attains the polarity value of the pure, more polar component at  $c_p^{\max}$ . This is illustrated in Fig.6.

This phenomenon is known for alcohols as "elevated polarity" (21) and for mixtures with chloroform as "synergetic polarity effect" (11).

Equation 3 holds even in this case. Within region I,  $c_p < c_k$ , and normal behaviour is observed (see Fig.7a). However, within region II nitromethane, which as pure substance is less polar, acts with 1-butanol like a more polar additive. Accordingly in this region there is a linear relationship between  $E_T(30)$  and  $\ln(c_u/c^* + 1)$ , where  $c_u$  is the molar concentration of the less polar component 1-butanol (see Fig.7b). By analogy to the previous examples, a virtual polarity can be defined for the polar component 1-butanol. Contrary to previous cases, however, it is greater than the actual polarity of the alcohol.

Here, also, two straight lines are observed. The second line, however, has a negative slope unlike in the previous cases. This can be explained by a hydrogen bond donor-acceptor model with the alcohol or chloroform as a hydrogen bond donor: the other component in each case as an additive, which itself has a low polarity, promotes the formation of a polar solvent structure. This behaviour is remarkable in so far as it contradicts the usual view that the polarity of a solvent mixture lies within the limits of its components; furthermore the polarity of solvents can be enhanced by adding less polar components.

## 6. SOLUTIONS OF ELECTROLYTES

The influence of the addition of electrolytes on the polarity of an organic solvent is an interesting problem, but has received little attention (25-28). The full charge separation of the ions could influence the solvent structure in a very profound manner. On the other hand, in media with low polarity, ion-pairs are formed by self-solvation which causes a lower interaction with the solvent. The effect of electrolytes on reaction rates is well-known as the "salt effect" (10,29) in mechanistic studies and has been attributed to the direct interaction of ions. However, the influence on solvent polarity should be examined.

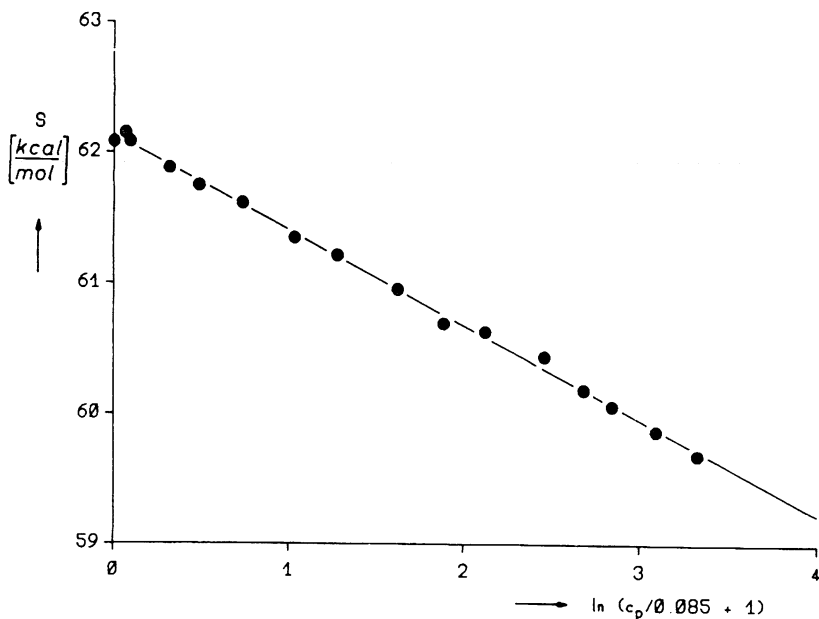
One main problem in the investigation of the polarity of solutions of electrolytes is the aggregation of polarity probes, for example dyes added to these media (25). The aggregation of dyes as H- and J-aggregates (30) with different types of stacking is well-known and cause a hypsochromic or a bathochromic shift of the uv/vis-absorption. This aggregation occurs even with dye chromophores as small as p-diethylaminonitrobenzene (**4**) (25), which is the basis for the  $\pi_1^*$  polarity scale (31) and excludes the use of this scale.

In order to overcome the problems with the dye aggregation (the pyridiniumphenolate betaine **1** of the  $E_T(30)$  scale aggregates too, as indicated by a change in line shape) the solvatochromic fluorescent dye **8** can be used, and this forms the basis of Zelinskii's polarity scale (32-34) S - the S values being calculated from  $\lambda_{\max}$  of the fluorescence according to equation 2.

Even dye **8** forms H-aggregates in electrolyte solution (25). However, fluorescence will not be obtained from H-aggregates, but from the non-aggregated molecules in equilibrium, as was pointed out by Förster (30). Because of this, the solvatochromism of isolated dye molecules can be studied in solutions containing electrolyte. The dependence of solvent polarity on the concentration of salt is given by equation 3 or 6, which hold even for electrolyte solutions.

### 6.1 Lithium Perchlorate in Acetic Acid

The special salt effect of  $\text{LiClO}_4$  in acetic acid is the experimental basis for the postulation of the solvent separated ion-pair (35). However, little is known about the influence of the salt concentration on solvent polarity. This can be investigated by the S scale mentioned above. The linear relation between S and  $\ln(c_p/c^* + 1)$  according to equation 6 is shown in Fig. 8.



**Fig.8:** Linear relationship between  $S$  and  $\ln(c_p/c^* + 1)$  for  $\text{LiClO}_4$  in acetic acid according to equation 7:  $E_D = -0.724$  and  $S^0 = 62.1$  kcal/mol, correlation coefficient  $r = -0.9987$  with 16 points,  $c_p$  and  $c^*$  in mol/l

A 2 molar solution of  $\text{LiClO}_4$  in acetic acid increases the polarity of solvent from  $S = 61.1$  to  $S = 59.8$ . This corresponds to 2 units on the  $E_T(30)$  scale. The effect is noticeable, but not high enough to explain the special salt effect.

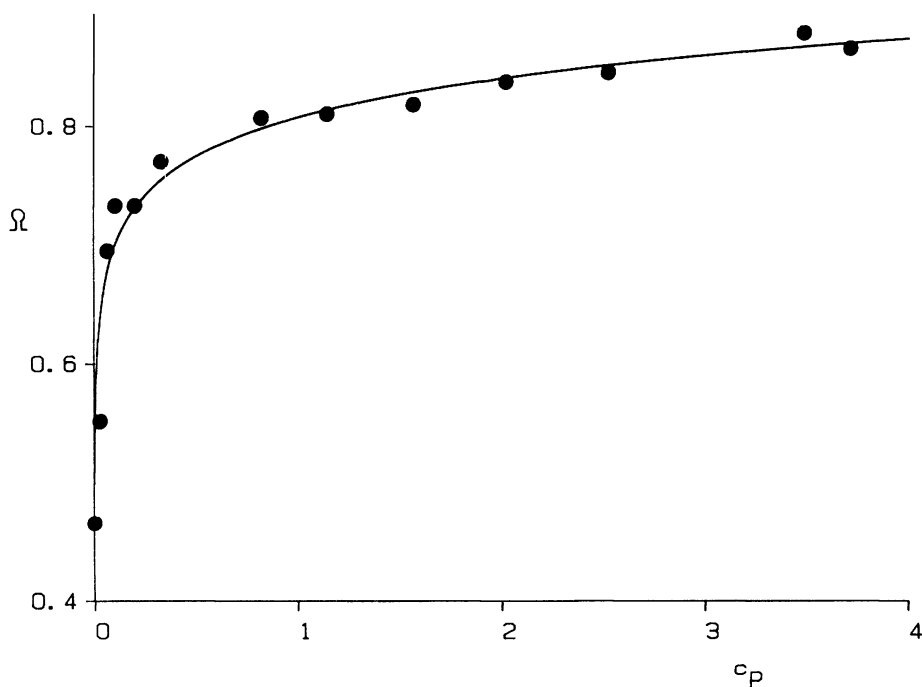
The linear correlation of Fig.8 can be used to extrapolate the straight line up to the concentration of pure  $\text{LiClO}_4$ . This would then be the polarity of  $\text{LiClO}_4$  if it were a liquid. An  $S$  value of 58.1 is obtained which characterizes it as a polar additive, but it is not as polar as water ( $S = 47.2$ ).

## 6.2 Lithium Perchlorate in Ether

Lithium perchlorate is very soluble in diethyl ether and solutions up to 6 M salt can be obtained (36,37). According to Pocker and Buchholz (38) (see also (39)) highly concentrated solutions of  $\text{LiClO}_4$  in ether can be regarded as fused salts



with small amounts of solvents added. Unusual reactivities are observed in these solutions - see for example (40-43). Surprisingly only little is known about the solvent polarity of this mixture. The first measurements were made by Sauer and coworkers (44) who applied the Berson  $\Omega$  scale (45). They obtained a curved functional line by plotting weight per cent  $\text{LiClO}_4$  against the  $\Omega$  values. This complex line can be analysed by the application of equation 6. Firstly, the weight per cent values of  $\text{LiClO}_4$  have to be converted to  $\text{mol}\cdot\text{l}^{-1}$ . This can also be done by the application of equation 6 (see below). A plot of the  $\Omega$  values against the molar concentration of  $\text{LiClO}_4$  is shown in Fig. 9.



**Fig.9:** The polarity of  $\text{LiClO}_4$ /ether mixtures (44) by  $\Omega$  scale as a function of the molar concentration (see below) of  $\text{LiClO}_4$ . - The function plotted is calculated by the application of equation 6 ( $E_D = 0.047$ ,  $c^* = 0.0015 \text{ mol/l}$ ,  $\Omega^0 = 0.499$ ,  $r = 0.973$ ,  $n = 13$ ).

The corresponding function 6 is plotted as a line in Fig.9. It is remarkable that the  $c^*$  value of the mixture is very low, and one can conclude from this that the

interaction of the solvated salt starts to take place even at very low concentrations. On the other hand, only one single relationship according to equation 6 is observed - no double straight lines. Therefore, the solvent structure is uniform up to a salt concentration of 40% by weight.

### 6.3 The Polarity of Alcoholic Electrolyte Solutions

The possibility of extending equation 6 even to solutions of electrolytes was first pointed out by Rezende and coworkers (26). They used the equation to give a quantitative description of the influence of salts on various chemical reactions (27) known in the literature. In further studies (28) the  $E_T(30)$  polarity scale was applied to the polarity of electrolyte solutions in the alcohols methanol, ethanol, 1-propanol, 1-butanol, and 2-butanol. The alkali metal salts LiCl, LiBr, LiI, NaBr, NaI, KI, LiClO<sub>4</sub>, NaClO<sub>4</sub> and the alkali earth salts Ca(ClO<sub>4</sub>)<sub>2</sub>, Sr(ClO<sub>4</sub>)<sub>2</sub>, and Ba(ClO<sub>4</sub>)<sub>2</sub> were investigated - equation 3 holds in all cases.

The parameters  $E_D$  and  $c^*$  of equation 3 vary considerably both with the nature of the salt and the alcohol (28). The parameter  $c^*$  decreases with decreasing polarity of the alcohol. This result is consistent with the fact that  $c^*$  is the concentration of salt at which the salt interaction must be taken into account - the lower the polarity of the alcohol, the lower is the concentration of salt at which the interaction becomes essential, for the solvation of the salt is getting worse. The  $c^*$  value varies only little with the nature of the cation when it is monovalent. With divalent cations the  $c^*$  value decreases markedly with decreasing ion size. This is consistent with the increasing surface charge of the ions and the increasing solvation demand. With the anions the effect is very similar - there is very little variation in the series; chloride, bromide and iodide anions give similar  $c^*$  values. Only the perchlorate ion, which has a very low polarizability, results in markedly lower  $c^*$  values.

The linear correlations according to equation 3 were extrapolated for the alcohol-salt-solutions up to the concentration of the pure salts given by their density and molecular weight. One might naively expect the same polarity for the same salt: regardless of alcohol, but this was not found - the calculated polarity of the pure salt depends on the alcohol used as second component. It decreases slightly with decreasing polarity of the alcohol. This might be due to a possible change in solvent structure (double straight lines) which would occur if one could increase the concentration of salt continuously from the pure solvent up to the pure salt. In

other words, a pure molten salt might have a completely different "solvent" structure from a diluted salt solution in some alcohol.

Nevertheless one can roughly calculate the polarity of the salts mentioned if they were pure liquids at room temperature. The calculated  $E_T(30)$  values are of the order of magnitude of the value for water.

## 7. SOLID SOLUTIONS

The solvent polarity is primarily defined for liquids and it is difficult to define a polarity for crystalline solids; for example, these solids have anisotropic properties and a polarity probe becomes a lattice defect. However, glasses have many things in common with liquids, for example their properties are usually isotropic.

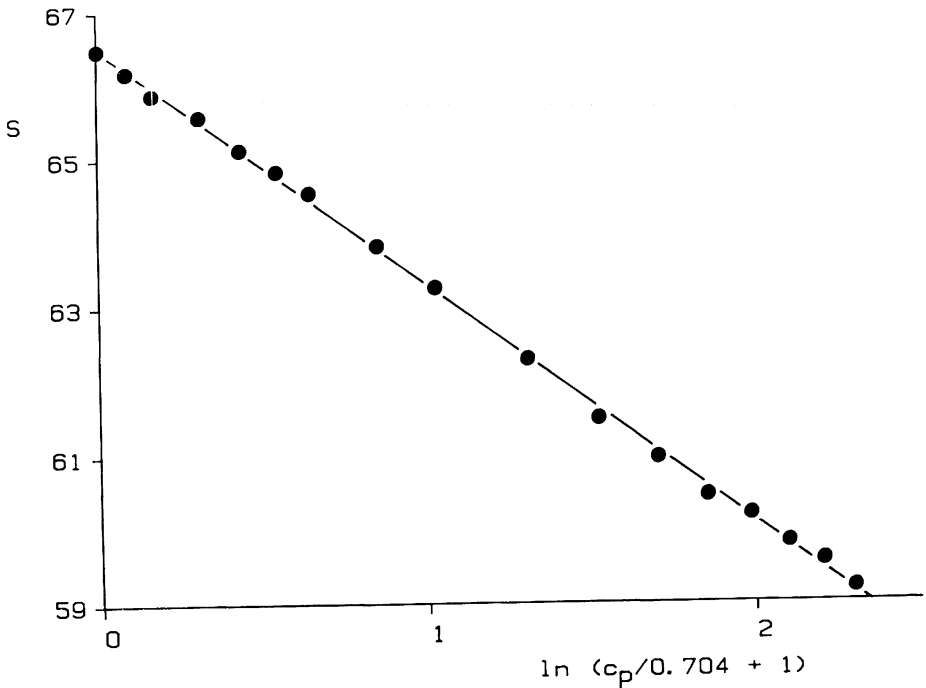
Organic glasses, for example poly(methyl methacrylate), can be examined with empirical polarity probes. The use of the  $E_T(30)$  polarity scale is difficult for this purpose because of the low solubility of dye **1** in the polymeric medium and the fact that a good optical quality of the solid sample is required for the absorption measurement.

Solvatochromic fluorescent dyes are to be preferred for the examination of solids, because fluorescent light can be detected with high sensitivity and the fluorescence of the sample being examined is a light source which can easily be focussed onto a detector. There are no problems with optical inhomogeneities. Therefore Zelinskii's S scale (32) with fluorescent dye **8** as a polarity probe is useful for solids. By the linear correlation between the S scale and the  $E_T(30)$  scale ( $E_T(30) = -1.93 \cdot S + 160.4$ ) the latter can be calculated for poly(methyl methacrylate) - an  $E_T(30)$  value of about 37 is obtained (46), which is similar to that of tetrahydrofuran.

The polarity of polymers is increased by polar additives. Both the influence of low molecular weight additives and copolymerisation are quantitatively described (46) by equation 6. Fig.10 is given as an example for the copolymerization between methyl methacrylate and the polar component 2-hydroxyethyl methacrylate.

The validity of measurements of the polarity of polymers is further established by the application of equation 6. Solvent orientation of liquids is replaced by chain reorientation in the solid or the reorientation of the low molecular weight

additives. In this way the empirically defined polarity of media is meaningful even for solids.



**Fig.10:** Polarity of the binary copolymer of methyl methacrylate and 2-hydroxyethyl methacrylate using the polarity scale  $S$ .  $c_p$  is the molar concentration of the unit 2-hydroxyethyl methacrylate ( $E_D = -3.193$ ,  $c^* = 0.704$  mol/l,  $S^0 = 66.5$ ,  $r = -0.9995$ ,  $n = 17$ ).

## 8. REGIONS OF LIMITED MISCIBILITY

The phenomenon of double straight lines (see section 5) is related to the formation of two distinct solvent structures. For binary mixtures between  $n$ -alcohols and water the influence of chain length of the alcohols on the polarity of the mixtures can be investigated (47). Double straight lines are obtained even with methanol as shown in Fig. 11.

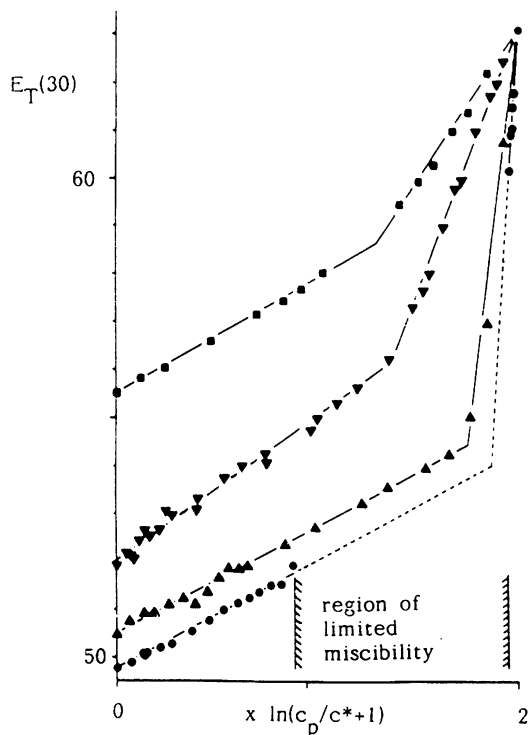


Fig.11:  $E_T(30)$  values of binary mixtures between n-alkanols and water as a function of  $\ln(c_p/c^* + 1)$  according to equation 1. - ■: Water/methanol ( $X = 0.157$ ); some values are taken from (4). - ▼: Water/ethanol ( $X = 0.318$ ); some values are taken from (4). - ▲: Water/1-propanol ( $X = 1.349$ ). - ●: Water/1-butanol ( $X = 1.705$ )

With methanol as a component with lower polarity the slope of the two lines is not very different, but this difference increases with the chain length of the alcohols. The longer the chain length of the alcohols, the less similar is the solvent structure to that of water and finally with 1-butanol two different phases are formed.

It can therefore be concluded that the formation of two solvent structures is not a function of limited miscibility and occurs even with lower alcohols. However, the formation of two separate phases is determined only by the surface tension between the two solvent structures - this is too small between lower alcohols and water to get two phases, but high enough with higher alcohols. This may be

additionally influenced by the fact that the two solvent structures are more similar in the case of lower alcohols than with higher alcohols.

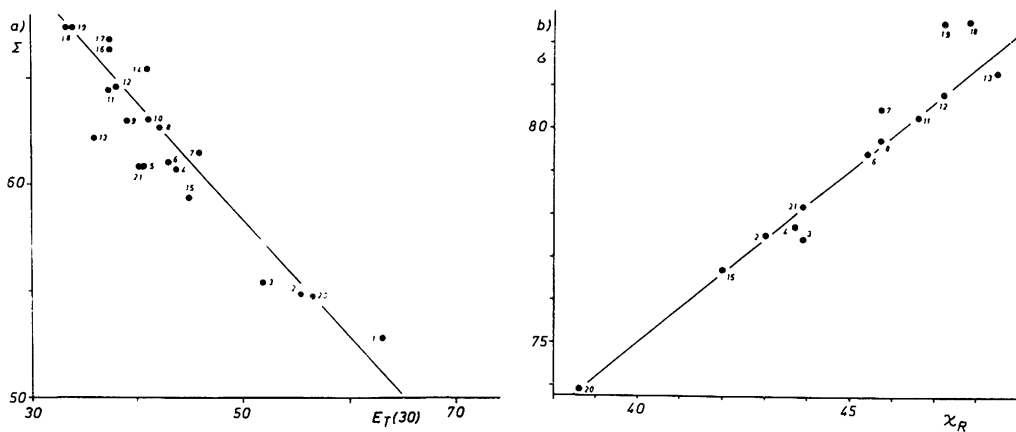
This behaviour described for binary mixtures of components with limited miscibility is not restricted to water as polar component. Binary mixtures of acetonitrile with octylbenzene or DMF with cyclohexane have essentially the same behaviour (48).

## 9. SLOW AND FAST PROCESSES

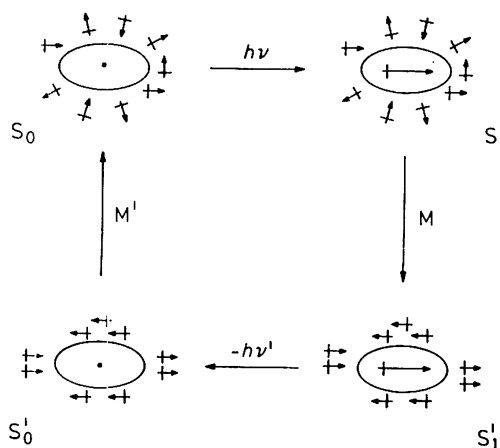
The majority of polarity scales show mutual linear correlation and with the  $Y$  and  $E_T(30)$  scales, as far as pure solvents are concerned. This fact is confirmed by principal components analysis (22,49) and by multi-parameter analysis (31). A few scales form an exception, but these also mutually correlate. This behaviour typically occurs with weakly polar merocyanines which have positive solvatochromism (10,50). One of the first cases to be studied was Brooker's (51)  $\chi_R$  scale, which is based on the solvatochromism of dye **7**. Polarity scales like  $\chi_R$  will be discussed extensively here, particularly their applications to binary solvent mixtures.

Studies of the solvatochromism of the phthalimide derivative **8** indicates that this exhibits strongly positive solvatochromism in fluorescence phenomena, and this was proposed as the basis for the  $S$  polarity scale by Zelinskii and colleagues (32-33); for the influence of oxygen see (34). The absorption by this dye is also solvatochromic (21). A linear relationship with the  $E_T(30)$  scale exists for fluorescence, but a linear relationship with the  $\chi_R$  scale is observed for absorption (see Fig.12). Thus, dye **8** is especially suitable for clarifying the previously mentioned exceptions, since it supplies a common basis for both groups of polarity scales.

It is known that the ground state ( $S_0$ ) of **8** has only a small dipole moment; however, the first electronically excited state ( $S_1$ ), has a large dipole moment (18). The different behaviour of **8** in absorption and emission can be explained by assuming that states with large dipole moments are strongly solvated by reorientation of polar solvents, whereas states with small dipole moments are solvated weakly by this effect: the Franck-Condon principle for electronic transitions applies to the solvating shell of a dye (52). The electronic transition takes place in such a short period of time that the solvation is unable to follow by reorientation of the solvent molecules.



**Fig.12:** Linear correlation between a) the fluorescence of dye **8** and  $E_T(30)$  and b) the absorption with  $\chi_R$  for pure solvents. The ordinates are calculated according to equation 2.



**Fig.13:** Schematic representation of absorption and emission processes of dye **8** in polar solvents.

Consequently the orientation of these will only influence solvation in the initial state of an electronic transition, but not the final state. The latter will still bear the solvating shell of the initial state, and can be stabilized only by polarization effects. Absorption and fluorescence of **8** proceed as given in the scheme in Fig.13.

The initial state,  $S_0$ , is little influenced by the polar solvents. The excited state,  $S_1$ , has a large dipole moment, but is surrounded by the solvating shell of the  $S_0$  state. Thus solvent polarization effects are crucial for absorption - by analogy to the  $\chi_R$  scale. Excitation is followed by relaxation of the solvating shell; the lifetime of the excited state ( $S_1$ ) of ca.  $10^{-8}$  to  $10^{-9}$  s is long enough to permit a more favorable orientation of the solvent molecules surrounding the dye molecules. The transition from  $S_1$  to  $S_1'$  corresponds to the modification (M) as described for reaction of the excited states in which the excitation energy is conserved (53,54,55-56). Finally the transition from  $S_1'$  to  $S_0'$  occurs by fluorescence, the energy of which is fully influenced by solvent orientation phenomena (besides polarization effects) because the dipole moment of the initial state of this electronic transition is large. It is therefore reasonable that the fluorescence of **8** correlates with the  $E_T(30)$  scale. The absorption of dye **1** is similar (1). However, in most cases the behaviour of other dyes is by no means as extreme as the absorption of **1** or **7**, and a combination of polarization and orientation effects is observed. These, furthermore, are not independent of each other, but interact. Frequently, however, the orientation effects prevail and this results in correlation with the  $E_T(30)$  scale. These considerations allow the conclusion to be made that dye **7** ( $\chi_R$  scale) is a polarity indicator for short measuring times, cf. the concept proposed by Bakhshiev (57). In organic chemistry the reorientation of the solvent, a relatively slow process, is of crucial influence. Thus, it is reasonable that such processes are correctly described by the  $E_T(30)$  scale.

Equation 6 characterizes the polar behaviour of binary liquid mixtures according to the  $\chi_R$  scale or to an absorption scale using dye **8** as a reference. Thus it can be concluded that equation 6 will also describe the polar behaviour of binary solvent mixtures in fast processes. Equation 6 cannot, therefore, be solely attributed to the concentration of the polar solvent on the surface of the dye (58-59). Further information on solvent structure is provided by comparing the  $c^*$  values of dye **8** in solvent mixtures for absorption and emission (21).



## 10. APPLICATIONS OF EQUATIONS 3 AND 6

The validity of equation 6 is well established for binary solvent mixtures and very different polarity scales. On this basis the equation itself can be used as a tool for the interpolation of  $E_T(30)$  values (60) or different other purposes, for example, for mechanistic studies.

### 10.1. Determination of Water in Water-Containing Solvents

The residual content of water in dried solvents is important for many chemical reactions, metallorganic reactions for example, and may determine yields, reaction products, and selectivities. There is no problem for solvents like ether which are commonly stored over alkali metals; however, a great number of very hygroscopic solvents such as dimethyl sulphoxide, dimethylformamide, or ethanol have to be stored neat or over molecular sieves. Generally for preparative work the water content of these solvents is unknown, especially when the samples are old. The Karl-Fischer titration (61) is a useful method for the determination of water, but the titration needs special equipment (dead-stop method) and "know-how". Further complications occur in the presence of redox systems. So this titration is not carried out as a standard procedure with preparative work.

A simple and uncomplicated method for the determination of water can be developed using the fact that water has a very high solvent polarity (e.g. with the  $E_T(30)$  polarity scale) compared with most solvents. So even small amounts of water can markedly increase the polarity of a solvent. This has been used by Dimroth and Reichardt (62) for the determination of water by the peak shift of dye **1**, which is very sensitive to the water content of a solvent sample. However, the relation between the peak shift and the water content gives very non-linear calibration plots. This handicap has prevented the general use of the method, although the calibration curves have been measured for some binary mixtures (4,8,62-63).

The problem with the non-linear plots can be solved by the application of equation 3 (64-68). This gives a further, and essential, simplification for the procedure of determining water. For practical applications, equation 2 and 3 are transformed to equation 7 with  $E^{\#} = 28590 \text{ [kcal}\cdot\text{nm]}/E_D$ .

$$c = c^{\#} \cdot \exp (E^{\#} / \lambda_{\max} - E^{\#} / \lambda_{\max}^{\circ}) - c^{\#} \quad [7]$$

$c$  in equation 7 is the concentration of water in g/l or mol/l corresponding to the dimension of  $c^{\#}$ .  $c^{\#}$  is the  $c^*$  value in the dimensions of  $c$ .  $\lambda_{\max}$  is the absorption wavelength of the pyridiniumphenolate betaine **1** in the water-containing solvent and  $\lambda_{\max}^{\circ}$  is the  $\lambda_{\max}$  value of the pure dry solvent.  $E^{\#}$  is given above. The parameters  $E^{\#}$ ,  $c^{\#}$ , and  $\lambda_{\max}^{\circ}$  are given in Table 3 for a number of frequently used solvents for the pyridiniumphenolate betaine **1**.

**Table 3:** Parameters of equation 7 and dye **1** for frequently used solvents at 20°C.

solvent	$c^{\#}$ mol/l (g/l)	$E^{\#}$ nm	$\lambda_{\max}^{\circ}$ nm	$E^{\#} / \lambda_{\max}^{\circ}$
acetone	0.664 (12.0)	7960	677.5	11.7
acetonitrile	0.293 (5.28)	10600	625.5	16.9
1-butanol	1.98 (35.7)	21500	574.1	37.4
tert-butyl alcohol	1.01 (18.2)	10100	660.3	15.3
N-tert-butyl- formamide	28.2 (508)	5830	567.3	10.3
tert-butylhydro- peroxide (69)	0.340 (6.13)	20100	575.3	34.9
dimethoxyethane	0.301 (5.42)	9530	748.4	12.7
N,N'-dimethylacetamide	5.28 (95.1)	5510	664.9	8.29

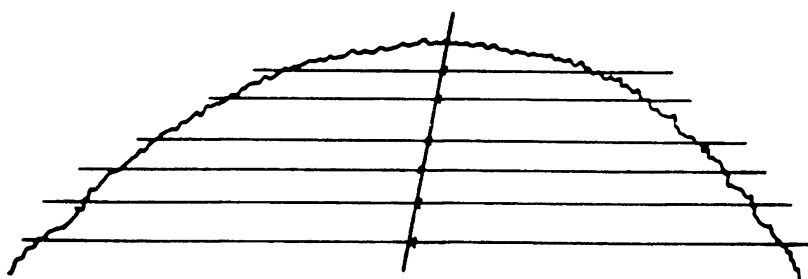
solvent	$c^{\#}$ mol/l (g/l)	$E^{\#}$ nm	$\lambda^{\circ}_{\max}$ nm	$E^{\#}/\lambda^{\circ}_{\max}$
DMEU <sup>a,b)</sup>	11.0 (198)	3010	672.7	4.47
1,4-dioxan	0.512 (9.22)	6600	794.2	8.31
DMF	11.52 (208)	2990	654.2	4.57
DMPU <sup>b,c)</sup>	12.8 (230)	2714	679.5	3.99
DMSO	53.8 (969)	1190	633.9	1.88
ethanol	38.1 (686)	4550	549.8	8.28
formamide	34.3 (618)	5120	511.4	10.0
HMPA <sup>d)</sup>	1000 (18020)	50.8	699.0	0.0727
methanol	150 (2700)	1600	516.1	3.10
2-methoxyethanol	12.4 (223)	15900	547.7	29.0
N-methylpyrrolidone <sup>b)</sup>	17.4 (313)	2320	677.5	3.42
nitromethane	1000 (18020)	6.92	617.5	0.0112
1-propanol	4.22 (76.0)	566.1	29.9	

solvent	$c^{\#}$ mol/l (g/l)	$E^{\#}$ nm	$\lambda_{\max}^o$ nm	$E^{\#}/\lambda_{\max}^o$
propylene carbonate	0.502 (9.04)	9264	621.5	14.9
pyridine	5.48 (98.7)	4030	711.2	5.67
THF	0.449 (8.09)	7090	764.4	9.28
TMU <sup>e)</sup>	4.02 (72.4)	4910	697.3	7.04

a) 1,3-dimethyl-2-imidazolidinone (70). b) substitute of HMPA. c) 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone - d) caution (71,72) - highly toxic! - e) tetramethylurea.

The determination of water can easily be carried out. - A small amount of the solvatochromic pyridiniumphenolate betaine is dissolved in the solvent sample so that the extinction of the long wavelength  $\lambda_{\max}$  of dye **1** lies between 0.7 and 1.0.  $\lambda_{\max}$  is determined and the content of water is calculated by means of equation 7 and the parameters of Table 3. The accuracy of the method depends only on the precision of the spectrometer and the magnitude of  $c^{\#}$  and is typically of the order of 5% at a water content of 10 g/l with spectrometers having 1 nm resolution. The sensitivity of the determination of water in acetonitrile which is obtained with such a spectrometer is for example 0.2 g/l. The  $c^{\#}$  value is important for the error of the determination. For  $c < c^{\#}$  the absolute error in the concentration determination is constant, whereas for  $c > c^{\#}$  the relative error is constant; for a more detailed discussion see (64-66).

For high precision water determinations the maximum wavelength ( $\lambda_{\max}$ ) must be measured with high accuracy. This could be done by the calculation of the first derivative of the uv/vis spectrum. However, this would result in a decrease of the signal to noise ratio of the spectrometer (73) and would give higher uncertainties in the determination method. Therefore, better results are obtained by applying Mathias' rule (74), which connects the half-radii of the secants according to Fig. 14. A calibration of the spectrometer should be done with holmium glass (75) and Mathias' rule directly before and after the determination.



**Fig.14:** The precise localisation of  $\lambda_{\max}$  of a broad absorption band by the use of Mathias' rule - the lines should be drawn in the region of 10 to 15 % from  $E_{\max}$ .

For a rough routine test for the water content of a solvent, a comparison of the colour of the dye solution with a colour scale of absorption wavelengths is sufficient and can give the wavelength to an accuracy of between 5 and 10 nm when the dye concentration is not very high and the person doing the test is

experienced in colour comparison. Colour scales, absorption wavelength and colour, are given, for example, in (76-77).

The parameters of equation 7 for frequently used solvents and dye **1** are given in Table 3. The parameters for further solvents can be easily measured in the known manner.

The validity of equation 3 is well established for a number of polarity scales; therefore the determination of water can be carried out with these other polarity probes. The advantage of dye **1** is the high sensitivity of the solvatochromism versus polarity. Therefore dye **1** should be used for all routine water determinations. Problems come about when the samples do not have good optical quality, for example turbid liquids; dye **1** should be replaced in these cases by the solvatochromic fluorescent dye **8** (66).

$\lambda_{\max}$  of the fluorescence can easily be determined even without a fluorescence spectrometer by a simple three-point-method (66). Equation 7 can also be applied for other physical effects. This has been done for the density and the index of refraction (65). With gases a concentration determination with an accuracy of 10 ppm is possible by a simple pressure measurement (66).

## 10.2. Analysis of Binary Mixtures

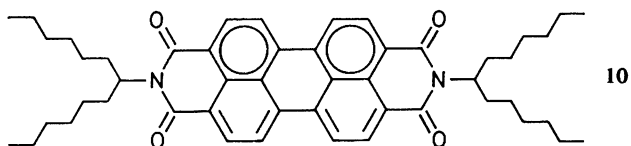
The validity of equation 7 is not limited to solvent mixtures involving water, but can be applied generally to binary solvent mixtures (65-66). The determination is more sensitive, the higher the polarity difference between the two components. Applications include, for example, the determination of solvent composition during continuous chromatography or column distillation.

## 10.3. Examination of Unusual Polarity Scales

### 10.3.1 Perylene Dyes as Polarity Probes

With the  $E_T(30)$  polarity scale the negative solvatochromism, or with the Y scale the rate enhancement of the solvolysis reaction, is taken as an indicator for the increasing polarity of a medium. There is no doubt about the direction of the effect, for it corresponds exactly to chemical experience and is a measure of the ability of the solvent to stabilize polar structures of a substrate by solvent reorientation (17). However, this is not so obvious when polarity scales are used which are sensitive towards other solvent effects. This is the case for the  $\chi_R$  scale of Brooker (51), the solvatochromism of dye **7**, which is more a measure of

the polarizability of the solvent than for the solvation effect by solvent reorientation (17).



This effect is even more pronounced with the polarity probe BHPD (bis-N,N'-(1-hexylheptyl)-perylene-3,4:9,10-tetracarboxylic-bisimide (78)), dye **10**, which has no dipole of the chromophore because of the point symmetry of the molecule. Due to the special structure of the dye, the solubility is so high that solvatochromism measurements are possible in a wide variety of solvents, from media with very high to very low polarity. The solvatochromism is not very pronounced, but can be measured with a precise spectrometer. Moreover the solvent effect can be checked by the investigation of the fluorescence. A decision as to what kind of solvents are polar for this dye is not simple, for there is no linear correlation of the energy of excitation with  $E_T(30)$  values, as is shown in Fig. 15 (correlation coefficient as low as  $-0.046!$ , 15 points). A solution of the problem (79) was possible by application of equation 3. A plot of the excitation energy ( $E_T(\text{BHPD})$ ) versus  $\ln(c/c^* + 1)$  gives a linear relation only when the concentration  $c$  of the polar component is used, but not with the concentration of the component with the lower polarity. The results of these measurements are given in Table 4 for pure solvents and in Table 5 for binary mixtures.

The solvatochromism of BHPD is very sensitive to polarizability effects of the solvent (79), but not very sensitive to dipole effects. Therefore, the  $E_T(\text{BHPD})$  values can be used as a novel polarity scale for these effects and might replace the  $\chi_R$  scale. The latter reflects mainly polarizability effects (17) of the solvent, but is still slightly influenced by solvent dipole effects.

**Table 4:** BHPD (dye 10) as a polarity probe for pure solvents

solvent	$\lambda_{\max}^{\text{a)}$ [nm]	$E_{\text{T}}(\text{BHPD})^{\text{b)}$ [kcal/mol]	$E_{\text{T}}(30)^{\text{c)}$ [kcal/mol]
cyclohexane	516.6	55.34	39.9
diethyl ether	517.4	55.26	34.5
acetone	519.2	55.07	42.2
acetonitrile	520.2	54.96	46.0
tetrahydrofuran	521.48	54.83	37.4
methanol	521.54	54.82	55.4
ethanol	521.81	54.79	51.9
1-propanol	523.25	54.64	50.7
1-butanol	523.5	54.61	50.2
1,2-dichloroethane	524.3	54.53	41.9
methylene chloride	524.3	54.53	40.7
dimethylformamide	525.5	54.41	43.8
chloroform	526.4	54.31	39.1
toluene	526.57	54.30	33.9
dimethyl sulphoxide	528.45	54.10	45.1
1-methylnaphthalene	541.15	52.83	35.3

a) Maximum of the long wavelength absorption. - b) Calculated from  $\lambda_{\max}$  according to equation 2. - c) See (1,4-6).

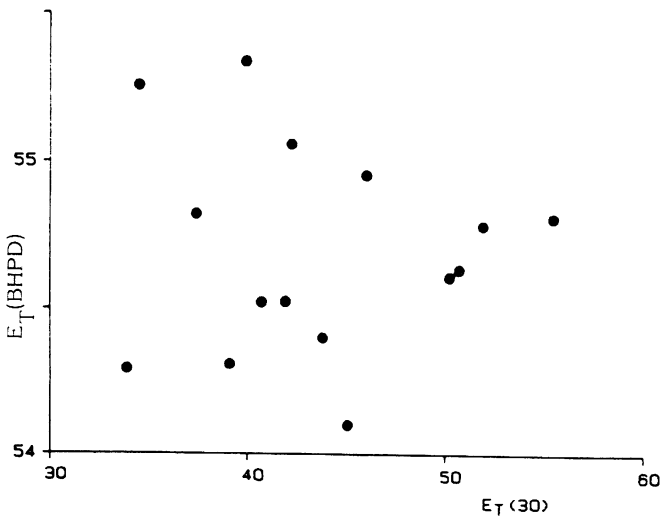


**Table 5:** BHPD (dye **10**) as a polarity probe for binary mixtures - application of equation 6 with  $P = E_T(\text{BHPD})$  at 20°C.

solvents <sup>a)</sup>	$E_D$ [kcal/mol]	$c^*$ [mol/l]	$E_T(\text{BHPD})^o$ [kcal/mol]	$r^{b)}$ $n^{c)}$	$c_k^{d)}$ [mol/l]
DMSO toluene	-0.085	0.103	54.37	-0.9974 23	8.45
DMSO THF	-1.413	24.06	54.79	-0.9963 21	
DMSO $\text{CH}_2\text{Cl}_2$	-0.503	10.91	54.53	0.9994 25	
DMSO acetone	-1.974	23.30	55.06	-0.9988 21	
DMSO DMF	-9.743	463	54.40	-0.9980 23	
DMSO ethanol	-13.3	328	54.81	-0.9974 20	8.45
DMSO methanol	-24.46	480	54.85	-0.9945 31	
1-methylnaphthalene toluene	-2.16	7.30	54.29	-0.99996 22	
1-methylnaphthalene THF	-3.861	10.14	54.84	-0.9994 21	
1-methylnaphthalene DMSO	-0.499	0.534	54.12	-0.9989 21	

solvents <sup>a)</sup>	$E_D$ [kcal/mol]	$c^*$ [mol/l]	$E_T(\text{BHPD})^0$ [kcal/mol]	$r^b)$ $n^c)$	$c_k^d)$ [mol/l]
1-methylnaphthalene ethanol	-1.295	0.558	54.80	0.9995	1.06
1-methylnaphthalene methanol	1.032	0.296	54.83	0.9991 21	0.63

a) The first component is the more polar/polarizable concerning the  $E_T(\text{BHPD})$  scale. - b) Correlation coefficient. - c) Number of points. d) Critical concentration for change in solvent structure.

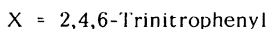
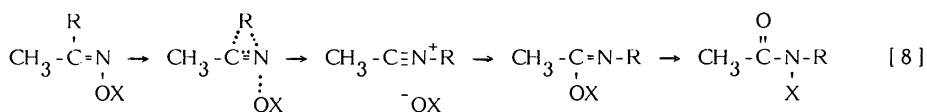


**Fig. 15:** Lack of correlation between  $E_T(\text{BHPD})$  and  $E_T(30)$  for the solvents of Table 4.

### 10.3.2 Sextet Rearrangements as Polarity Probes

New polarity scales can be developed on the basis of reaction kinetics to measure solvent effects on microscopic processes. The Y solvent polarity scale of Winstein and Grunwald (3) on the basis of the solvolysis reaction of tert-butyl chloride has been a very important tool, both for the study of reaction mechanisms and for practical applications; see for example (1,10). Later on it turned out that there are problems with this polarity scale, for it is limited to very polar solvents. Moreover there were mechanistic problems caused by different ion-pairs acting as intermediates, reversibility of the elementary steps, and specific solvation of the nascent ions, see for example (29). Therefore secondary polarity scales on the basis of spectroscopic measurements were favoured. A generally applicable polarity scale on the basis of a chemical reaction would be a good supplement to the other polarity scales. The Berson  $\Omega$  scale (45), which takes as a measure the solvent dependence of a Diels-Alder Reaction, is only partially useful for this purpose, because it is a bimolecular reaction and therefore principally sensitive to aggregation phenomena (26). Moreover there is no ionization in the rate-determining step.

On the other hand, the rate constant of the Beckmann rearrangement (80) is strongly solvent dependent. The mechanism of the Chapman-variant (81) of the Beckmann rearrangement, the thermal reaction of ketoxime picrates, has been thoroughly studied (82-88). The reaction pathway for anti-methylketoxime picrates, which can easily be prepared (84-88), is given by equation 8.



The rate-determining step of the reaction is the migration of R with the formation of a nitrilium ion (89). The reaction is followed by two fast steps - the recombination of the ion-pairs and the final formation of the N-picrylacetyl amides.

The rate constant of the Chapman-variant of the Beckmann rearrangement might be especially useful as a solvent polarity probe and has been used already by Fischer (90) for the investigation of solvent effects. It is important therefore that

the rate-determining step, the ionisation, is an irreversible reaction (80) - the strongly negative reaction enthalpy of  $-80$  kcal/mol (91) and an activation enthalpy of about  $30$  kcal/mol for the alkyl migration are additional indications that an endothermic step during the reaction should not be allowed. Another advantage is that in the transition state of the reaction there is a separation between the positive partial charge, which is mainly concentrated in the migrating alkyl group (88), and the negative charge on the leaving group; this averages solvent effects and makes specific solvent effects less probable. Finally the large molar coefficient of extinction allows reaction kinetic measurements at high dilution and so the solvent is only little perturbed by the polarity probe.

Alkyl and aryl substituents are possible as migrating groups. The alkyl migration should be chosen to exclude the possible formation of  $\pi$ -complexes with aromatic systems. To exclude further any possible backside solvation of the migrating group one can use bridgehead substituents which exclude such an attack of a nucleophile. In order to have a test for specific solvent effect one can compare the solvent effect on bridgehead derivatives of very different structures.

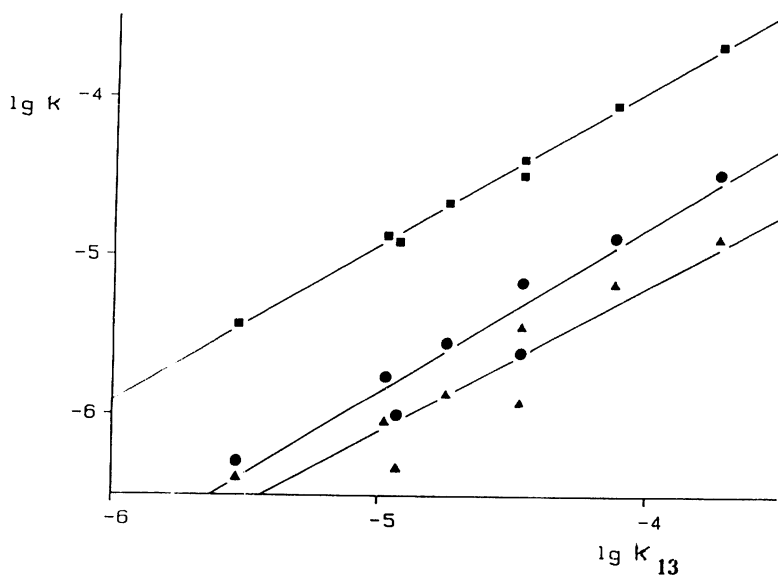
**11****12****13****14**

The rate constants for the migration of the oxime picrates with these groups (92) in very different solvents are given in Table 6.

It can easily be seen that the ratio of the migration aptitude of the substituents **11** ... **13** is about constant for different solvents. This is demonstrated by Fig. 16.

**Table 6:** Solvent dependence of the rate constants ( $k \cdot 10^7 [s^{-1}]$ ) of methylketoxime picrates at 25°C

subst. R:	1-bicyclo- [2.2.2]octyl (11)	1-bicyclo- [3.2.1]octyl (12)	1-adamantyl (13)	1-bicyclo- [3.2.2]nonyl (14)
methanol (1)	35.2	88.8	338.3	396.7
ethanol (2)	13.41	28.3	180.0	180.0
1-butanol (3)	9.03	17.5	107.8	133.3
DMSO (4)	125.7	321.7	1833	2083
DMF (5)	65.3	128.3	750.0	876.7
CH <sub>2</sub> Cl <sub>2</sub> (6)	11.85	24.7	336.7	313.3
CHCl <sub>3</sub> (7)	4.67	10.01	116.7	120.3
THF (8)	4.05	5.15	29.5	36.8



**Fig.16:** Linear correlation between  $\lg k$  of **13** and  $\lg k$  of **11**, **12**, and **14** for different pure solvents (see Table 6).

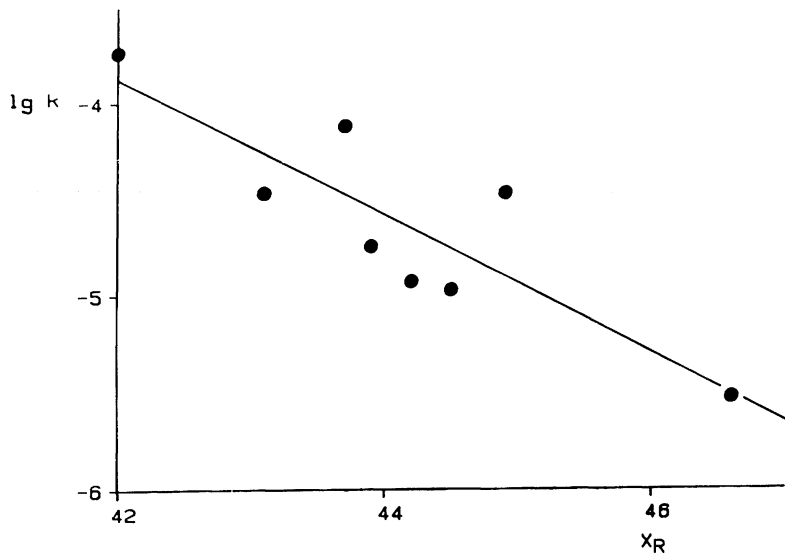


Fig.17: Linear correlation between  $\lg k$  of the Beckmann rearrangement of **13** and the  $X_R$  values of Brooker (51).

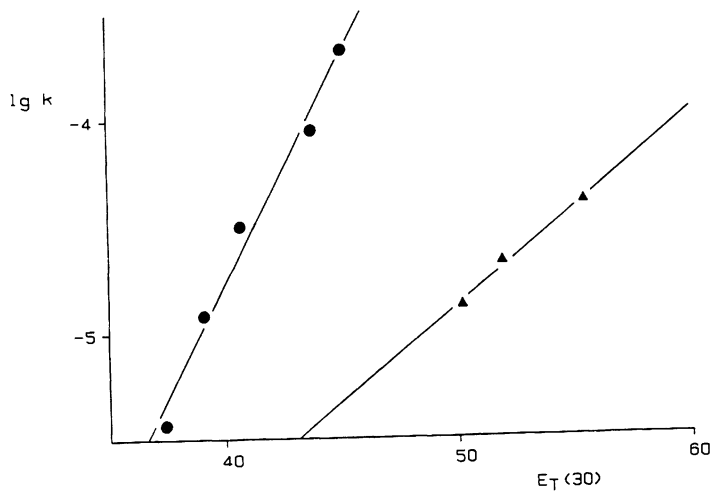


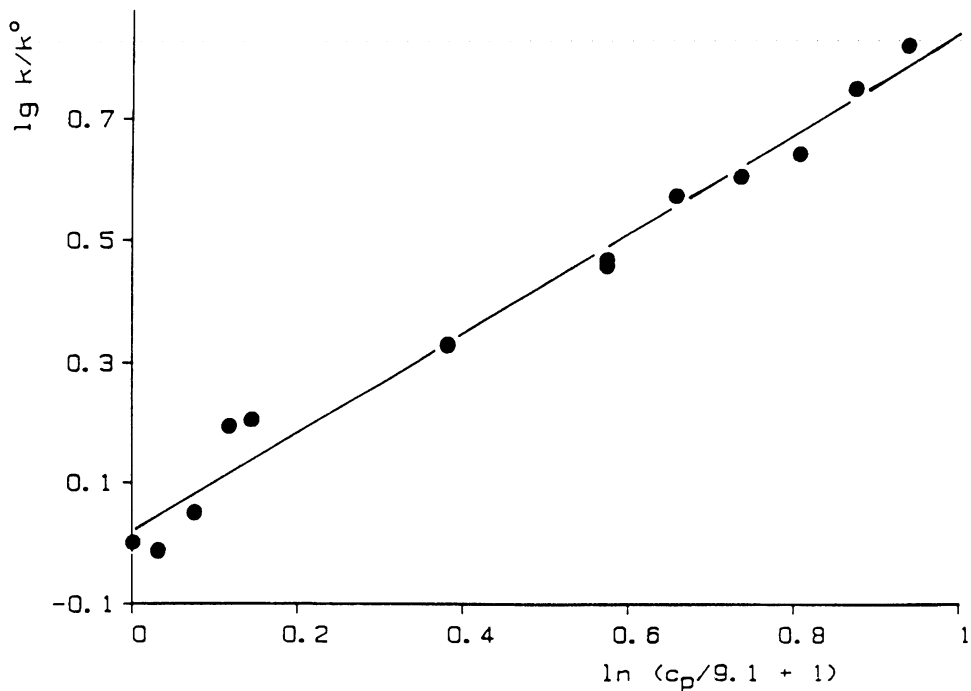
Fig.18: Linear correlation between  $\lg k$  of the Beckmann rearrangement of **13** and the  $E_T(30)$  values of Dimroth and Reichardt (6) - ▲: alcohols ( $\lg k = 0.09 \cdot E_T(30) - 9.4$ ;  $r = 0.994$ ), ●: other solvents ( $\lg k = 0.21 \cdot E_T(30) - 13.3$ ;  $r = 0.990$ ).

So specific solvent interactions with the substrates are essentially excluded. On the other hand, the rearrangement is very fast in DMF and DMSO (nr. (4) and (5) of Table 6). It was shown in earlier work that these solvents act mainly by their large microscopic polarizability (17,21). A useful measure of these effects is the  $\chi_R$ -solvent polarity scale of Brooker (51) - the reasonably good correlation with this polarity scale is given in Fig.17. On the other hand, solvent orientation phenomena are important too; this is demonstrated by the linear correlations of Fig.18. However, not a single linear correlation is obtained, but two: one for alcohols and another one for the other solvents. This is in contrast to the single good linear correlation of the  $E_T(30)$  scale with the  $Y$  scale of the  $S_N1$  solvolysis reaction of tert-butyl chloride. A possible explanation for these differences is given by the fact that with the solvolysis reaction the charge separation in the transition state is localized on only a few atoms; see (93) for a further discussion of the solvation of the educt. This can be efficiently solvated by the reorientation of the solvent, and especially by polar solvent structures like the  $O\cdots H-O-$  hydrogen bond structure of alcohols. In contrast, with the Beckmann-Chapman rearrangement the charge separation in the transition state is spread over a large number of atoms, see equation 8. In this case solvation by the orientation of solvent molecules and by the polar hydrogen bonding is not so efficient as with  $S_N1$ -type solvolysis reactions. So for alcohols one obtains the second straight line of Fig.18, at lower values of  $\lg k$  and not as steep. The polarizability of the solvent is of greater importance for the solvent stabilization of the spread charge - therefore, the linear correlation with the  $\chi_R$  scale is obtained. This result could be important also for other reactions, for example for  $S_N2$  reactions, and could explain the strong rate enhancement effect (94) which is observed in some cases, when even small amounts of DMSO are added to polar protic solvents, for example to water.

Finally, the possibility should be excluded that the high reaction rate of the Beckmann rearrangement in DMSO or DMF is not due to complexation. This can be done by the application of equation 3. To this end, the rate constant of the rearrangement of **13** is measured in the binary mixture methylene chloride/DMSO as a function of the composition. Equation 3 is transformed to equation 9.

$$\lg \frac{k}{k_o} = E_D \lg (c_p/c^* + 1) \quad [9]$$

$k$  is the rate constant for the rearrangement in the mixture and  $k^0$  in the pure component with lower polarity (methylene chloride). The other symbols of the equation have been defined previously. With equation 9 a linear relation between  $\lg k/k^0$  and  $\ln (c_p/c^* + 1)$  is obtained.



**Fig.19:** Linear correlation between  $\lg k/k^0$  and  $\ln (c_p/c^* + 1)$  according to equation 9 for the mixture  $\text{CH}_2\text{Cl}_2/\text{DMSO}$  (oxime picrate **13**).

The linear correlation in Fig.19 ( $E_D = 0.863 \text{ kcal}\cdot\text{mol}^{-1}$ ,  $c^* = 9.73 \text{ mol}\cdot\text{l}^{-1}$ , correlation coefficient 0.991 for 14 points) indicates a normal solvent effect by DMSO. The  $c^*$  value as an indicator for the interaction with the more polar component ranges from medium to large, see (17), just as for a normal solvent effect.

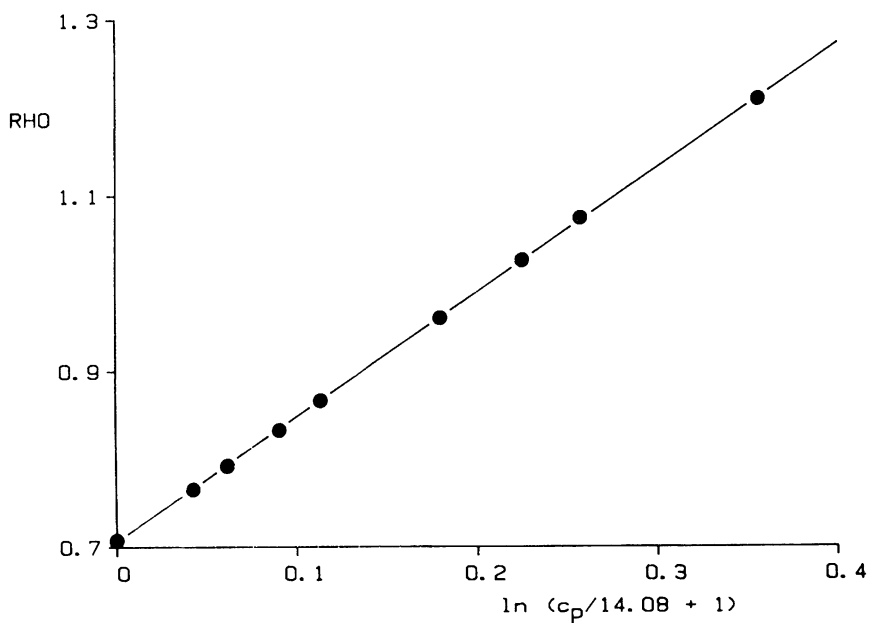
#### 10.4. Calculation of Molar Concentration from Weight Percentages

Concentrations in binary mixtures are often given in the literature in weight %. For many purposes, for example for the application of equation 3 or 6, the molar



concentration of one component is required and this can be calculated from the density of the mixture. However, in many cases the densities at only a few concentrations are known.

The problem can be solved by the application of equation 6, which holds also for the densities of binary mixtures (67). This is demonstrated for the example  $\text{LiClO}_4/\text{Ether}$ , in which the concentrations of  $\text{LiClO}_4$  were needed for polarity measurements (see above). The densities for nine salt concentrations were taken from (37) and plotted against  $\ln(c_p/c^* + 1)$  as in Fig. 20.



**Fig.20:** Densities of solutions of  $\text{LiClO}_4$  in ether (37) as a function of  $\ln(c_p/c^* + 1)$  with  $c_p$  as the molar concentration of  $\text{LiClO}_4$  ( $E_D = 1.414293$ ,  $c^* = 14.08$  mol/l,  $\rho^0 = 0.706135$ ,  $r = 0.99996$ ,  $n = 9$ ).

With the linear correlation of Fig. 15 the density of a solution of  $\text{LiClO}_4$  in ether can be calculated directly and from this the content in weight % is found with high precision.

The converse calculation of the concentration from weight % is more complicated. Therefore equation 6a has to be transformed to equation 10 with MW as the molecular weight of  $\text{LiClO}_4$  and G the content by weight.

$$\rho = E_D \ln (c_p/c^* + 1) + \rho^0 \quad [6a]$$

$$c_p \cdot \text{MW}/G = E_D \cdot \ln (c_p/c^* + 1) + \rho^0 \quad [10]$$

$$\delta = E_D \cdot \ln (c_p/c^* + 1) + \rho^0 - c_p \cdot \text{MW}/G \quad [11]$$

Equation 10 cannot be solved directly to give the concentration in closed form, but by the transformation to equation 11 the concentration can be iteratively determined using a computer program which minimizes the residue  $\delta$ .

## 10.5. Studies of Reaction Mechanisms

### 10.5.1 Solvolysis of tert-Butyl Chloride in Ethanol-Water

The discovery of the Winstein relationship (3), which is based on the solvolysis of tert-butyl chloride, played a key role in the development of the empirical polarity concept. Subsequently Winstein studied the influence of temperature on the solvolysis of tert-butyl chloride in ethanol/water mixtures (95). The free energy of activation,  $\Delta G^\ddagger$ , of this reaction increases as a monotonic function, without strong curvature, as the water content of the mixture is increased: the course of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , however, is more complex and maxima and minima occur (see Fig.21).

This unusual and surprising behaviour led to numerous speculations (10,23,93,96-101) and an explanation has been given in (17). It seems to contradict experience that the  $\Delta G^\ddagger$  value, which is composed of enthalpy and entropy terms, has a simple functional course, whilst the apparently simpler quantities  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  appear so complicated. Since the solvolysis of tert-butyl chloride is sensitive to polarity changes in the medium, an analysis of Winstein and Fainberg's measurements using equation 6 appears appropriate. As shown in Fig.22, the free enthalpy of activation  $\Delta G^\ddagger_{298}$  of the solvolysis of tert-butyl chloride in ethanol/water mixtures and the

correspondingly proportional quantities in  $k_{298}$  or  $Y$  can be described quantitatively by equation 6 as a function of composition.

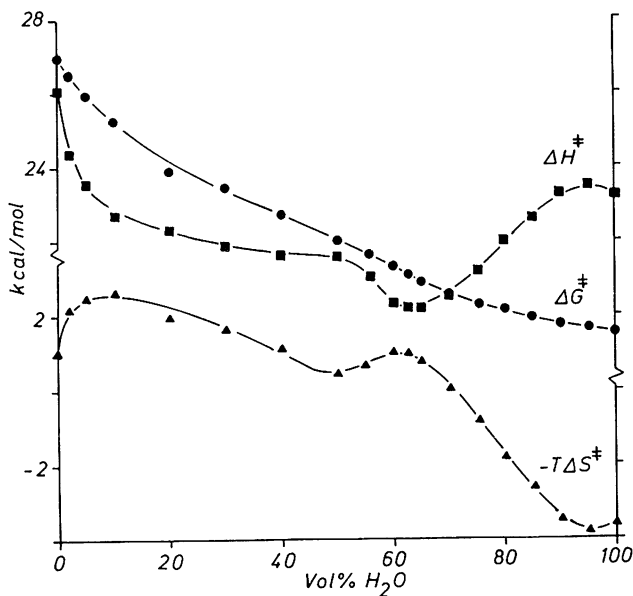
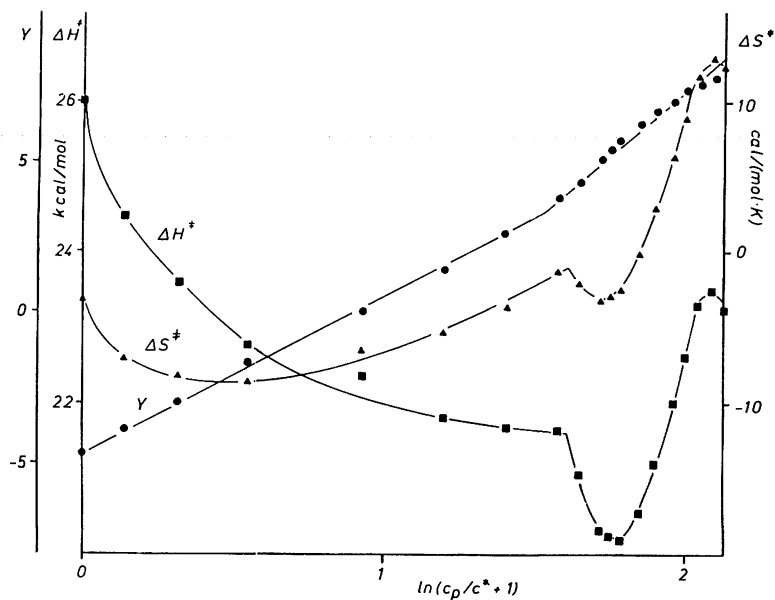


Fig.21: Thermodynamic data for the solvolysis of tert-butyl chloride in ethanol-water (95).

An interesting point is, as with other polarity scales (see section 5), that two regions of validity of equation 6 are observed with a critical transition point at  $c_k \approx 25$  mol/l (double lines). Thus the free enthalpy of activation shows nothing anomalous. The high precision of Winstein's kinetic measurements must be stressed; this is expressed by the conformity of the experimental points to the lines in Fig. 22.

The activation enthalpy  $\Delta H^\ddagger$  and the activation entropy  $\Delta S^\ddagger$  of the reaction were calculated from the rate constants at only two temperatures (95); in the range 0 to 45 vol. % water at 25<sup>o</sup> and 50<sup>o</sup>C and in the range of 50 to 100 vol. % water at 0<sup>o</sup> and 25<sup>o</sup>C. It can be shown that equation 6 holds for the series of

measurements at 0°C and 50°C (see Table 7); their  $E_D$  and  $c^*$  values are only slightly different from the measurements at 25°C.



**Fig.22:** Analysis of solvolysis data of tert-butyl chloride in ethanol-water according to equation 6.

**Table 7:** Application of equation 6 to the Winstein scale.

$T^a)$	Range <sup>b)</sup>	$E_D^c)$	$c^{*d)}$	$\gamma^o e)$	$r^f)$	$N^g)$
25	I	2.9	11.6	-1.79	0.9991	9
50	I	2.4	9.7	-0.52	0.9998	7
0	II	2.6	0.001	(-26.9)	0.9845	12
25	II	2.7	0.001	(-26.1)	0.9935	10
$(\Delta H_T^\ddagger)^b)$	I	-0.944 <sup>i)</sup>	0.26	(26.1) <sup>h,i)</sup>	0.9996	6

a) Temperature in °C . b) See text. c) In Y units. d) mol/l. e) extrapolated Y value for ethanol. f) Correlation coefficient. g) Number of points. h) Activation energy. i) In kcal/mol.

The change of temperature from 0° to 50°C for the calculation of the activation data was conducted in water concentrations of ca. 25 mol/l (the second temperature was 25°C in all cases). By chance this value coincides approximately with the value of  $c_k$  corresponding to the intersection point of the two lines in Fig. 22. Based on this the course of the functional curve of  $\Delta H^\ddagger$  in Fig. 21 can be characterized.

For  $c_p < c_k$  (region I,  $\Delta H^\ddagger - \ln k_{298} - \ln k_{323}$ ),  $\Delta H^\ddagger$  is a monotonic function of the water content. The  $E_D$  and  $c^*$  values of  $\ln k$  are only slightly different at 25° and 50°C. Thus even the solvent dependence of  $\Delta H^\ddagger$  is approximately described by equation 6 (table 7). In this correlation the expansion of the liquid must be taken into account, since at a given concentration in vol % the molar water content is temperature dependent.

In the region  $c_p \approx c_k$  a number of factors cause  $\Delta H^\ddagger$  to have a rather complex dependence on concentration. Going beyond  $c_k$ , the temperature dependence of composition and the temperature change have the effect that the individual measurements for determining  $\Delta H^\ddagger$  are made partly in region I and region II. This results in the unusual functional course of  $\Delta H^\ddagger$ .

Finally, in the region  $c_p > c_k$  (region II) a monotonic dependence of the  $\Delta H^\ddagger$  values on the solvent composition is observed, as in region I. The additional maximum at very high water content may be a result of mixing problems and will not be discussed here; this is dealt with in (96,102). The concentration dependence of  $\Delta S^\ddagger$  (Figs. 22 and 23), can be explained in an analogous manner to the difference between  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$ .

The solvolysis of tert-butyl chloride in ethanol-water, discussed here at length, is characteristic of other solvolysis reactions in solvent mixtures (23,101-102,103-104), which can be treated in a similar way, and is also generally typical of mechanistic studies in them. Furthermore the reference point of the Y scale, 80 vol % ethanol/water, may present problems if the temperature differs substantially from 25°C.

Another result of the previous analysis is of general interest: for reactions influenced by the polarity of the medium, the free energy of activation,  $\Delta G^\ddagger$ , should, at least in solvent mixtures, be a simpler parameter than  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , since these always contain contributions from the thermal expansion of the liquid

which are not reaction-specific. Special attention is therefore required when a solvent mixture exhibits two regions of validity of equation 6 (cf. also section 5).

#### 10.5.2 Non-linear Winstein Relationships

The results just mentioned lead to other applications of equation 4 to mechanistic studies: linear correlation of a process with the Winstein relationship is often used as a mechanistic criterion, by analogy to other linear free energy (LFE) relationships, e.g. see (3,105-108). In the first place the value  $m$ , the slope of the straight line, is interpreted as a measure of the sensitivity of the reaction studied to solvent polarity effects and is often related to increase or decrease of charge separation leading to the transition state. Furthermore, a linear correlation over a large range of solvent polarity is used as an indication of uniform reaction mechanism in different solvents. In order to obtain a sufficient number of measurements, reactions are usually studied using solvent mixtures, often ethanol-water.

As the polarity of these mixtures is governed by equation 6, it seems worthwhile to redefine the previously mentioned mechanistic criteria on the basis of equation 6.

From equation 6, the slope  $m$  of a relationship between two polarity-dependent processes  $P_1$  and  $P_2$  is described by equation 12.

$$m = \frac{dP_1}{dP_2} = \frac{E_{D1}(c_p + c^*_2)}{E_{D2}(c_p + c^*_1)} \quad [12]$$

A good linear relationship between  $P_1$  and  $P_2$  requires that the slope  $m$  in equation 12 is independent of  $c_p$ , and hence one of the following three conditions must be fulfilled:

1. The  $c^*$  values of both processes are similar ( $c^*_1 \approx c^*_2$ ). The terms of equation 12 in brackets are very similar and the slope is concentration independent. The logarithmic term in equation 6 has an approximately equal numerical value in both cases for a given value of  $c_p$ . Consequently,  $P_1$  and  $P_2$  are linearly dependent.
2. The  $c^*$  values are different in both cases, but considerably larger than  $c_p^{\max}$  ( $c^*_1, c^*_2 \gg c_p^{\max}$ ). The  $c_p$  values in equation 12 become small compared

- to the  $c^*$  values for any experimentally possible concentration and the slope becomes concentration independent. Equation 6 can be expanded both for  $P_1$  and  $P_2$  as a Taylor series, which as usual is truncated. A linear relationship between  $P$  and  $c_p$  results, and likewise a linear relation between  $P_1$  and  $P_2$ .
3. The  $c^*$  values are different, but both very small compared with experimentally relevant concentrations. Equation 12 can be simplified by neglecting the  $c^*$  values and  $m$  becomes independent of  $c_p$ . In each case  $P$  and  $\ln c_p$  are linearly dependent and therefore also  $P_1$  and  $P_2$ .

One of these three conditions is often fulfilled. However, if a non-linear relationship is found, e.g. with the Winstein scale, it does not necessarily follow that there is a change in mechanism, or even that a continuous transition from one mechanism to another occurs upon varying the medium, cf. also (109). This information is only obtained by estimating the  $c^*$  values.

Even more complicated is the influence of the solvent and its dependence on  $c_p$  when mixtures with critical transition points (double lines) are used. These are observed particularly when solvolysis reactions are carried out in frequently-used binary mixtures such as acetone-water, 1,4-dioxan-water and ethanol-water (see Table 2) (19,65). An example for the mixture ethanol-water is described here.

Bentley, Brown and coworkers (110) studied the solvolysis of isopropyl, cyclohexyl, and 2-adamantyl tosylates in ethanol-water. The free energies of activation show good linear correlation with the Y scale up to a water content of ca. 50%. At higher water contents, substantial deviations are observed, which represent a regular break in the LFE relationship, Fig. 1 in (110). Nucleophilic solvent participation with a change in reaction mechanism was discussed. This appears to be contradicted by the behaviour of isopropyl tosylate, which, because it is hardly shielded and easily accessible to nucleophilic attack, shows the smallest deviations. These were finally attributed to a specific solvation of the leaving anion, since the corresponding mesylates show linear relationships with the Y scale.

The solvolysis data can be analysed on the basis of equation 6. The break in LFE relationship is observed at a water content of ca. 50% and can be interpreted as a critical transition point (see section 5). Since similar  $c^*$  values are found for the solvolysis of tert-butyl chloride (Y scale) and the various tosylates, a discussion of the  $E_D$  values according to equation 12 is sufficient. For tert-butyl chloride and

cyclohexyl mesylate (Table 8, Nos. 1 and 2), the ratio of the  $E_D$  values is almost equal in region I and II. Thus an approximate LFE relationship is observed for the entire water concentration range. The relatively low  $E_D$  value of No. 2 even explains the slight deviations at high water contents.

**Table 8:** Solvolysis (95,110) in solvent mixture at 25°C.

No.	Substrate	Region I			Region II		
		$E_{DI}$	$c^*_I$	$\ln k_{0I}$	$E_{DII}$	$c^*_{II}$	$\ln k_{0II}$
		a)	b)	c)	a)	b)	c)
1	tert-Butyl chloride	6.7	11.6	-16.1	6.3	0.001	-7.16
2	Cyclohexyl mesylate	4.7	10.8	-17.3	4.6	(0.001) <sup>d)</sup>	-
3	2-Adamantyl tosylate	4.7	8.3	-21.6	9.9	0.001	-11.7
4	2-Propyl tosylate	3.2	12.9	-14.7	5.0	(0.001) <sup>d)</sup>	-
5	Cyclohexyl tosylate	8.3	32.8	-16.8	7.7	0.001	-9.1

a) In  $\ln k_{298}$  units. b) In mol/l. c) Value for pure alcohol extrapolated from equation 6. d) Estimated, since too few points are available for calculation.

The tosylates, however, behave quite differently (Table 8, Nos. 1,3, and 4). The much higher values of  $E_D$  in region II result in LFE relationships whose slopes are almost twice as large as those in region I. Therefore, breaks in the relationships must exist at  $c_k$ , Fig. 1 in (110). The  $c^*$  value of cyclohexyl tosylate (Table 8, Nos. 1 and 5) no longer coincides with that of No.1. Appropriately the resulting LFE relationship is considerably worse. In this case a simple comparison of the  $E_D$  values is not sufficient. Detailed analysis, however, shows, that No. 5 behaves in the same way as Nos. 3 and 4. The solvolysis reaction in acetone -water mixtures can be analysed in an exactly analogous manner.

Sridharan and Vitullo (108) studied the solvolysis of geminal dihalides in 1,4-dioxan-water. Here, also, the LFE relationship with the Y scale turned out to be non-linear, with two straight lines. This was attributed to a change of reaction mechanism and transition to nucleophilic solvent participation. It can be shown,



however, that the critical transition point of 1,4-dioxan-water mixtures coincides with the point of intersection of the two lines.

The last examples show that the existence of an LFE relationship is only a limited mechanistic criterion for studying solvent dependent processes in solvent mixtures. Therefore, when examining such processes, binary mixtures should be checked for critical transition points.

### 10.6 Further Applications

By means of equation 3 or 6 the polarity of a medium can be exactly adjusted to a problem, when reaction mechanisms are different in polar or non-polar media. An example is the thermolysis of percarboxylic esters, for a review see (111), which, in non-polar media, generally proceeds homolytically with radical formation; in polar media, however, heterolysis occurs according to the Criegee mechanism. If generation in polar media is desired, it is advantageous to adjust the polarity of the medium to a point at which homolysis just prevails.

In other cases, where the addition of a small amount of polar additive should enhance the solvent polarity as much as possible (53),  $c^*$  plays a key role. If  $c_p < c^*$ , the polarity is strongly dependent on  $c_p$ , but if  $c_p > c^*$  this is true only to a small extent (the relationship is roughly logarithmic). In order to employ a minimum of polar additive,  $c_p$  should be adjusted to approximately  $c^*$  (if  $c^*$  is small).

Other applications are in chromatographic methods, where small amounts of polar additive increase the polarity of a solvent markedly, or are in polymer chemistry where one can get more information about the parameters of copolymerization by the application of the knowledge about binary mixtures.

## 11. OUTLOOK - FURTHER EXTENSIONS

Apart from the previously described areas of chemistry, equation 6 can be utilized in many others which can only be mentioned briefly here. For the polymer chemistry, equation 6 might be very useful, e.g for the planning and investigation of copolymerisates, additives of polymers and polymer blends.

Another field is the extension of the equation to ternary and even more complex mixtures. Initial experimental results demonstrate that this is in principle possible though there are compensating effects (112).

Finally, the equation might be extended even to explain the polarity of a single pure substance. This has been demonstrated for pure gases (66) and n-alkanols (113). The latter can be thought to be a binary mixture of the polar OH-group with the hydrocarbon residue. If one calculates the molar concentration of the OH-groups in pure alcohols from molecular weight and density the same behaviour as with a binary mixture of alcohols and aliphatic hydrocarbons (113) is found.

One might expect to be able to calculate the polarity of a pure substance from increments of its polar functional groups. These calculations, however, are non-linear.

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