

UNUSUAL POLARITY BEHAVIOR OF BINARY LIQUID MIXTURES

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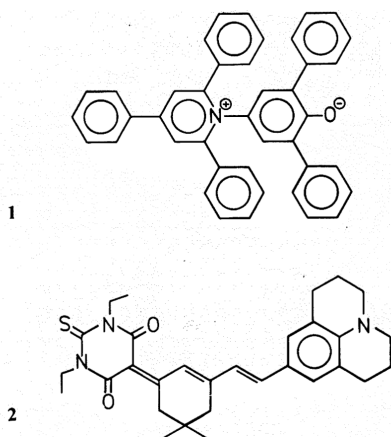
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ABSTRACT. - With mixtures of short-chain alcohols and dipolar aprotic solvents an elevation of polarity is observed within a definite composition range. By means of a two-parameter-equation it is shown, that in each case one component of the mixture affects the other with a virtual polarity, which is larger than the actual value. The results are interpreted using a donor-acceptor-model and applications are discussed.

ABRISS. — Bei Mischungen kurzkettiger Alkohole mit dipolar aprotischen Lösungsmitteln wird in einem bestimmten Konzentrationsbereich eine Überhöhung der Polarität beobachtet. Mit Hilfe einer Zwei-Parameter-Gleichung wird gezeigt, dass jeweils eine Komponente der Mischung auf die andere mit einer virtuellen Polarität wirkt, die größer als der tatsächliche Wert ist. Die Ergebnisse werden im Rahmen eines Donor-Acceptor-Modells interpretiert, und Anwendungen werden diskutiert.

A much-discussed question is how to describe the polarity of a liquid quantitatively¹⁻³. Since macroscopic physical quantities such as the dielectric constant or the refractive index are only relatively crude measures of polarity²⁻⁴, a number of purely empirical polarity scales based on solvent-dependent processes have been developed recently. One of the most widely used and comprehensive polarity scales today is the $E_T(30)$ scale^{1,5} developed by Dimroth and Reichardt, which is based on the strong negative solvatochromism of the pyridinium-*N*-phenolate betaine **1** (CAS RN 10081-39-7).



It can be used to correctly describe many solvent-dependent processes.

It is important for understanding the polarity phenomenon that the commonly used polarity scales are linearly correlated with each other and with the $E_T(30)$ scale^{2,6,7}. As a consequence, it must be

concluded that a generally valid, but so far only empirically graspable, polarity measure exists and that one of these scales can be used to study polarity effects in a representative manner.

$$P_G = E_D \cdot \ln \left(\frac{c_p}{c^*} + 1 \right) + P_G^0, \quad (1)$$

Previous work⁸⁻¹³ has succeeded in quantitatively describing the polarities of binary liquid mixtures as a function of their composition using the universal two-parameter equation (1), in which P_G is the polarity of the solution [for **1**, $P_G = E_T(30)$] and c_p is the molar concentration of the more polar component [the component with the higher $E_T(30)$ value]. E_D (energy penetration) and c^* (appearance concentration) are the parameters of Equation (1)⁸ and P_G^0 is the P_G value of the pure lower polar component. The $E_T(30)$ values, i.e., the molar excitation energies of **1**, are calculated from λ_{\max} of its solvatochromism band using Eq. (2):

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

The validity of Eq. (1) has been demonstrated for numerous binary liquid mixtures (about 50 so far)¹⁰ using various polarity scales¹¹ P_G . It also confirms the common view that the polarity of a binary mixture lies within the limits of the polarities of its two components. In the literature, monotonic curves have also been obtained in the vast majority of cases when polarity is plotted against the composition of binary mixtures^{2,5,14}. However, it has been observed by Maksimovic, Reichardt, and Spiric in mixtures of,

for example, chloroform with ketones, sulfoxides, and trialkyl phosphates that in a certain concentration range the polarity of these binary mixtures is larger than that of the individual components¹⁷. This has been termed the synergistic polarity phenomenon^{2,17}.

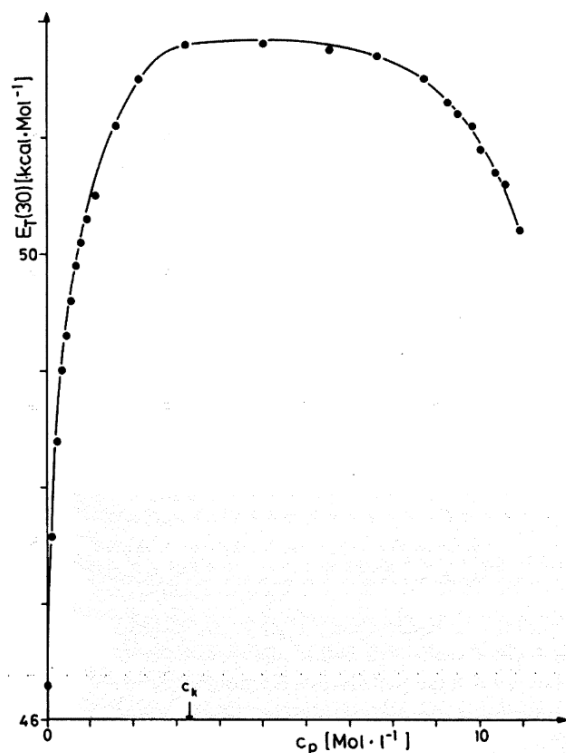


Figure 1. - Polarity of the 1-butanol-nitromethane mixture as a function of the 1-butanol content.

Results

Mixtures between 1-butanol and nitromethane, for example, deviate from the usual polarity behavior described above. If the polarity of these is plotted against the composition, e.g. as an $E_T(30)$ value, as in Figure 1, curves are obtained which pass through a maximum.

This means that in a certain concentration range the mixtures are more polar than the pure components. In the following, this unexpected polarity behavior will be investigated in more detail using Eq. (1). As can be seen from Figure 2a, at the left branch of the curve ($c_p < c_k$) of Figure 1, normal behavior of a mixture satisfying Eq. (1) is present (partially straight curve in Figure 2a for the mixture 1-butanol-nitromethane).

It is noteworthy, however, that the right branch of the curve ($c_p > c_k$) in Figure 1 also satisfies equation (1) (see Figure 2b). The straight line obtained in this concentration range according to Eq. (1) is shown in Figure 2b. c_p in Eq. (1) must then be replaced by c_u , the concentration of the minor polar component (analogously, c_k then becomes c'_k). However, the E_D and c^* values are different from the former (see Table). Thus, in the region of the right-hand branch of Figure 1, the component nitromethane, which is minor polar as a pure substance, increases the polarity of the mixture in the same way as a more polar additive. An increase in polarity is not only observed for the mixture 1-butanol-nitromethane, but, as can be

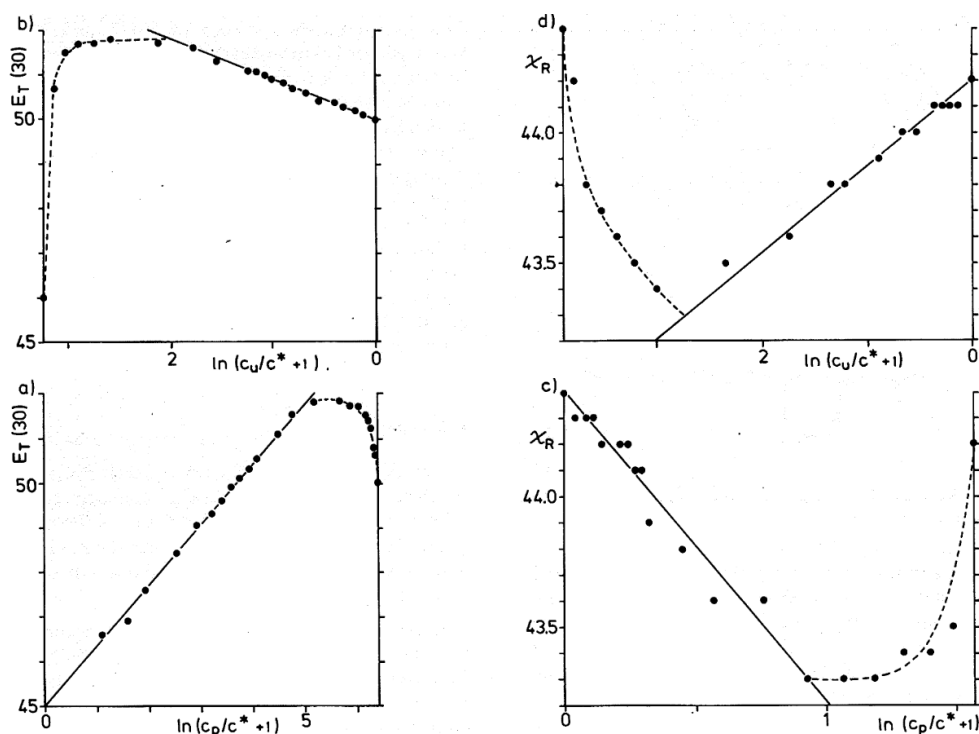


Figure 2. - Relationship between P_G and (a, c) $\ln(c_p/c^* + 1)$ or (b, d) $\ln(c_u/c^* + 1)$ for solvatochromic dyes 1 (a, b) and 2 (c, d) dissolved in 1-butanol-nitromethane.

Table. - Polarity excesses of binary liquid mixtures.

Mixture ^a	Dye	$c^*{}^b$	E_D^c	r^d	n^e	$P_G^{0c,f}$	$P_G^{\text{max},c,g}$	$P_v^{c,h}$	$c_k^{b,i}$	$P_G(c_k)^{c,g}$	$APE^{c,k}$
Methanol-acetonitrile	1	0.06	1.83	0.99838	31	46.0	55.5	57.0	19.8	56.6	1.1
Ethanol-acetonitrile	1	0.05	1.69	0.99971	31	46.0	51.9	55.9	6.8	54.3	2.4
1-Hexanol-acetonitrile	1	0.08	1.08	0.99786	29	29.0	46.0	48.8	-	-	-
Butandiol-1,4-acetonitrile	1	0.01	1.53	0.99749	31	46.0	55.5	-	-	-	-
Methanol-DMF	1	0.70	3.55	0.99745	31	43.8	55.5	-	-	-	-
Ethanol-DMF	1	0.61	2.78	0.99792	31	43.8	51.9	53.2	13.8	52.6	0.7
1-Butanol-DMF	1	1.64	3.20	0.99935	30	43.8	50.2	50.3	8.7	50.3	(0.1)
Ethanol-DMSO	1	2.69	3.95	0.99794	30	45.0	51.9	52.9	13.8	52.4	0.5
1-Butanol-DMSO	1	4.29	4.93	0.99475	30	45.0	50.2	51.2	7.7	50.6	0.4
Methanol-nitromethane	1	0.01	1.66	0.99947	29	46.3	55.5	59.3	7.4	55.8	0.3
Ethanol-nitromethane	1	0.03	1.41	0.99704	30	46.3	51.9	55.2	6.9	54.0	2.1
1-Butanol-nitromethane	1	0.02	1.33	0.99924	31	46.3	50.2	54.7	3.3	51.8	1.6
(Nitromethane-1-butanol ^l)	1	0.75	0.87	0.99831	31	50.2	46.3	53.0	3.7	51.8	1.6
Ethanol-TMU	1	0.81	3.51	0.99925	31	41.0	51.9	-	-	-	-
1-Butanol-TMU	1	0.91	3.56	0.99936	31	41.0	50.2	-	-	-	-
1-Butanol-nitromethane	2	2.86	-1.15	-0.98776	31	44.4	44.2	42.6	4.4	43.3	-0.9
(Nitromethane-1-butanol ^l)	2	0.40	-0.27	-0.99382	31	44.2	44.4	43.2	5.6	43.3	-0.9

^a The more polar component is listed first; ^b in mol·L⁻¹; ^c in kcal·mol⁻¹; ^d correlation coefficient according to Eq. (1); ^e number of points; ^f polarity of the less polar component; ^g polarity of the more polar component; ^h virtual polarity (see text); ⁱ critical concentration; ^j maximum polarity (at c_k); ^k see text; ^l inverse mixture.

seen from the table, is typical for mixtures between aliphatic alcohols with about four C atoms and dipolar aprotic solvents¹⁵.

Discussion of the results

The described unusual polarity behavior of mixtures between alcohols and dipolar aprotic solvents is interpreted with the following model: The components are known to be typical hydrogen bond donors and acceptors, and such interactions are expected to affect the properties of the liquid mixed phases. The polarity of the alcohol is determined partly by the nonpolar alkyl radical and partly by the polar alcohol function. Addition of the acceptor, which is less polar on its own, forces the polar donor-acceptor structure and leads to the observed increase in polarity. Thus, the acceptor addition acts like the addition of a more polar component and finds its quantitative description in Eq. (1). However, once the polarity maximum is reached at c_k , a further addition to the less polar component only has a diluting effect and one finally observes the normal behavior⁸ of a binary mixture. As can be seen from Fig. 2, one component of the binary mixture exerts a higher polarity-increasing effect on the other up to the concentrations c_k and c'_k , respectively, than would be expected from the polarities of the pure substances. In the range $c_p < c_k$ or $c_u < c'_k$, they simulate an increased polarity, which is called virtual polarity, P'_v in the following, and whose calculation is permitted by Eq. (1) if the molar concentrations of the pure polar and nonpolar components are used for c_p and c_u , respectively. They can also be seen from the Table. Towards nitromethane, for example, 1-butanol exerts a polarity approximately as strong as propane-1,2-diol, and nitromethane acts on 1-butanol like butane-1,3-diol.

The table still shows the absolute polarity increase APE . This is the amount by which the binary mixture at c_k is more polar than the more polar component.

At the $E_T(30)$ scale, dye **1**, no reversal of solvatochromism¹ (transition from negative to positive solvatochromism) occurs even in the most polar solvents known. Since in the mixtures studied even these polarity values in the range of c_k are far from being reached, the observed phenomenon is clearly an effect of the medium and not of the dye. Another indication is that the unusual polarity behavior occurs not only with the $E_T(30)$ scale, but is also observed with the Brooker χ_R scale, dye **2** (RN 2913-22-6), as can be seen from Figure 2c and d. Moreover, the experimentally determined concentrations c_k are about the same for both polarity scales. These agreements are noteworthy because deviations from linear correlation with the other polarity scales were observed just for the χ_R -scale^{2,7,16}.

Further insight is provided by examining the chain length influence of the alcohol component on the absolute polarity increase or the difference between actual and virtual polarity. As can be seen from the table, the strongest polarity increases (APE or $P_D - P_{C_{\text{max}}}$) are observed for alcohols with two to four C atoms (cf. e.g. ethanol-acetonitrile, ethanol-nitromethane and 1-butanol-nitromethane). For shorter-chain methanol, this effect decreases (e.g., methanol-acetonitrile and methanol-nitromethane), and it disappears completely for long-chain alcohols (1-hexanol-acetonitrile). No polarity enhancement is found for the divalent alcohol butane-1,4-diol (when mixed with acetonitrile). This result can be understood to mean that polar structures already predominate in the case of shorter-chain or polyhydric alcohols and that

relatively strong acceptors are therefore necessary for a polarity enhancement. For alcohols with a chain length around C4, the polarity should be equally influenced by the less polar alkane residue and the alcohol function. In this case, it is expected that the polarity can be increased very efficiently, even if only relatively weak acceptors are added. Finally, in the case of long-chain alcohols, the influence of the decidedly low-polarity alkane chain predominates.

Consistent with this interpretation of the polarity behavior is the observation that the polarity exaggeration is relatively large when using strongly polar dipolar aprotic solvents such as acetonitrile or nitromethane, while it is significantly smaller with less polar acceptors such as DMSO or DMF. Finally, for the even less polar tetramethylurea (TMU), no polarity exaggeration is observed.

The described effect of polarity enhancement has consequences for preparative work and also mechanistic investigations, which will only be briefly touched upon here. For example, it is known ² that even small additions of dipolar aprotic solvents to polar protic ones can cause considerable increases in reactivity and yield. This observation, not yet fully understood, may be related to the model presented. There is also the possibility of producing mixtures from low polar components that are highly polar. Such mixtures could be used in syntheses where pure polar solvents interfere. For example, one goal would be to obtain solvent mixtures that are more polar than water. Furthermore, the present results are of importance for the modification of the properties of polymers. These problems are currently still in progress and will be dealt with elsewhere.

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Experimental section

The dyes **1** and **2** used have been synthesized according to Lit. ^{5,7}. The determination of E_D and c^* of Eq. (1) has been carried out at 25°C using the UV spectrometer DMR 21 from Zeiss completely analogous to Ref. ⁸. The calculation of the published data was carried out with the help of the computer program POLAR ⁸ at the computer center of the University of Freiburg.

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