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CONTRIBUTION OF ACTIVITY COEFFICIENTS TO THE NUCLEOPHILICITY OF SOLVENT COMPONENTS IN SOLVENT MIXTURES. INFLUENCE OF ADDED ACETONE ON SELECTIVITY VALUES, k_E/k_W, IN ETHANOL–WATER MIXTURES

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Literature data on the change in the selectivity values, k_E/k_W, for several solvolysing systems in ethanol (E)–water (W) on addition of acetone were analysed. It is suggested that acetone acts as a basic cosolvent for both ethanol and water and that the change in the activity coefficients on changing the solvent composition is mainly responsible for the observed effect.

INTRODUCTION

A common method for studying nucleophilic substitutions at carbon and the nature of possible intermediates involves a measurement of the selectivity of the electrophilic centre towards different nucleophiles. This is frequently done in order to provide information pertinent to the reactivity–selectivity principle (RSP).[1] When two nucleophiles (Nu′, Nu″) attack a common electrophile (RX or a solvolytically generated R^+), the selectivity (S) is usually obtained from the products distributions:

$$S = k_{Nu'}/k_{Nu''} = [RNu'][Nu'']/[RNu''][Nu'] \quad (1)$$

For the competitive reaction of N_3^- and H_2O with alkyl chlorides, Sneen *et al.*[2] and Raber *et al.*[3] found a linear $\log k_{N_3^-}/k_{H_2O}$ vs. $\log k_{solv}(RCl)$ relationship in 80% acetone. This is a reactivity–selectivity behaviour since $\log k_{solv}$ was taken as a measure of the stability and hence of the reactivity of R^+. A reinvestigation showed that an extended relationship is not linear.[4]

Relevant data on selectivity towards two competing nucleophilic solvent components can be found or calculated from the literature. The most common pair of nucleophiles is ethanol (E) and water (W), and selectivity values k_E/k_W are known for a wide range of electrophiles from the relatively stable p-$Me_2NC_6H_4CH^+(CH_3)$[5,6] to primary alkyl substrates.[7–9] Most of the literature data are fragmentary and difficult to systematize, but RSP behaviour was observed in some series. Several problems which might cause the k_E/k_W values calculated by equation (1) to differ from the true selectivity measures were discussed.[10] The reaction of 1-arylethyl carbocations with alcohols, including EtOH, in 50 : 50 CF_3CH_2OH–H_2O shows a regular but complicated change in the selectivity as a function of the ring substituent.[5] For four Ar_2CHCl, Karton and Pross[11] found that the plots of $\log k_E/k_W$ vs. σ^+ in several E–W mixtures are linear and parallel. Similar trends were found also by Harris *et al.*[12] and McLennan and Martin.[10] For $ArCH_2Cl$, Aronovitch and Pross[13] found a decrease in k_E/k_W values on increasing σ^+ in 95% E–W, but at lower ethanol concentrations there was no clear trend.

A major problem is the simultaneous change in solvent properties (i.e. dielectric constant, ionizing power, etc.) and in the concentrations of the nucleophilic solvent components. Hence, the selectivity towards two nucleophilic solvent components, calculated as in equation (1), almost always changes with the solvent composition.[10–21] For the E–W pair the k_E/k_W values decrease when the concentration of E increases. A typical example is the diarylmethyl system with various ring substituents and nucleofuges,[10,11] where k_E/k_W ratios decrease regularly by 30–50% on changing the solvent from 70% to 95% E–W[11] or from 50% to 80% E–W.[10] Although the effect is small, the regularity of the change in the k_E/k_W values points to their mechanistic significance.

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EFFECT OF ADDED ACETONE ON THE SELECTIVITY VALUES

In order to evaluate the contribution of the solvent ionizing power Y to the change in the selectivity values when the E content of E–W is varied, Pross and coworkers[7,11,13,14] and McLennan and Martin[10] investigated the influence of added acetone (A) on the k_E/k_W values of several solvolysing systems. Addition of A to E–W should change only the solvent properties at a constant E/W ratio. The suggestion that acetone could serve as a nucleophile, giving the intermediate $(CH_3)_2{=}\overset{+}{O}R$[22] seems a remote possibility in E–W.

Pross and co-workers' results[7,11,13,14] (Table 1) display the interesting feature of a similar decrease in the k_E/k_W values for diphenylmethyl, benzyl, octyl and adamantyl derivatives when the acetone volume percentage increases (the ratios of the selectivities at 0% and 80% acetone are between 1·6 and 1·9). p-$MeC_6H_4CH_2Cl$ in 50 : 50 E–W is an exception (ratio of 1·1), probably owing to a change in the product-forming step on changing the solvent composition.[13] For all these substrates, excluding the adamantyl systems, the decrease mainly parallels the decrease in the k_E/k_W values when [E] in E–W increases.[7,11,13] The k_E/k_W values for 1- and 2-adamantyl are insensitive to the concentration of E in the binary mixtures.[14] The similarity of the acetone effect is remarkable since the various systems solvolyse by different mechanisms and the product-forming species differ markedly in both structure and energy.

Pross and Karton[14] attributed the change in the selectivity values with the solvent composition primarily to 'a change in the relative nucleophilicities of ethanol and water as the solvent composition is varied' rather than to substrate–solvent interactions. They also suggested that acetone 'enhances water nucleophilicity relative to ethanol nucleophilicity,' but later they emphasized that the nucleophilicity of a solvent component is substrate dependent. This means that 'front side nucleophilicity,' which dominates product formation from the adamantyl solvent-separated ion pair ($k_E/k_W < 1$), and 'back side nucleophilicity,' which determines the selectivity in diphenylmethyl, benzyl and octyl substrates ($k_E/k_W > 1$), might respond differently to changes in the binary E–W mixtures, as was indeed found.

OPEN QUESTIONS

The conclusion[14] that solvent effects on the nucleophilic solvent components are responsible for the selectivity variations seems to be well founded, especially if each of the systems concerned solvolyses mainly through a single, although different, intermediate.[7,13,14] However, several questions are still left open: (i) what is the nature of the interaction between acetone and ethanol or water?; (ii) why is the effect similar for different mechanisms of nucleophilic substitution with different molecular requirements?; (iii) why do only the adamantyl systems react differently on adding acetone and on adding ethanol to E–W? We would expect that when products are formed, mainly by a back side attack of a solvent on an intimate or solvent-separated ion pair as in diphenylmethyl, benzyl and octyl halides,[7,13] the selectivity will be determined by the electron-donating power of the nucleophile. In contrast, when products originate from front side collapse of an irreversibly formed solvent-separated ion pair as in the adamantyl systems, the selectivity is largely determined by the relative ability of the solvent molecule in $R^+ | SOH | X^-$ to stabilize X^- by hydrogen bonding.[14,18,23]

A PARTIAL QUALITATIVE EXPLANATION

Symons' work[24,25] seems to be relevant to these questions. He suggested that in mixtures acetone acts as a basic cosolvent for both ethanol and water,[24] scavenges

Table 1. Selectivity values (k_E/k_W) in the presence of increasing acetone (A) concentrations (% v/v)

System	T/°C	EtOH : H_2O (v/v)	k_E/k_W in acetone solution[a] 0% A	20% A	40% A	60% A	80% A	Ref.
Ph_2CHCl	25	50 : 50	3·84[b]	3·56	3·24	2·78	2·44	11
$PhCH_2Cl$	75	50 : 50	3·33	2·88	2·59	2·18	1·73	13
	75	95·5	1·86	1·73	1·56	1·35		13
p-$CH_3C_6H_4CH_2Cl$	75	50 : 50	2·00	1·87	1·90	1·90	1·79	13
	75	95 : 5	1·91	1·64	1·52	1·36		13
n-$C_8H_{17}Br$	120	50 : 50	1·73	1·48	1·30	1·12	0·91	7
	120	90 : 10	1·03	0·87	0·85	0·79	0·78	7
1-Adamantyl-Br	75	60 : 40	0·57	0·53	0·49	0·45		14
2-Adamantyl-OTs[c]	75	60 : 40	0·58	0·51	0·45	0·40	0·32	14

[a] Solutions prepared using X% A and $(100 - X)$% E–W.
[b] Extrapolated from values at higher %E using the linear $\log(k_E/k_W)$ vs Y plot.[11]
[c] Very similar results were obtained for 2-adamantyl p-nitrobenzenesulphonate.[14]

free hydroxyl groups (OH_f) and thereby increases the concentration of free nucleophilic lone pairs (LP_f). Water and ethanol react preferentially via these units, however, in his words, 'because of the presence of weakly basic lone pairs on every alcohol molecule, the extra catalytic effect of free lone-pair groups (caused by a basic cosolvent) is less pronounced (for ethanol) than for aqueous systems.' These suggestions might explain the role of acetone in E–W mixtures for diphenylmethyl, benzyl and octyl halides but not for the adamantyl systems. Still, Symons found that methanol added to water acted also as an OH_f scavenger,[24] and since adding acetone to E–W means partial replacement of both of them, the total effect might be complex. In addition, Symons' concepts were developed and checked at molar fractions of cosolvents below 0·2 which correspond to 45% ethanol or 50% acetone in water or 24% acetone in ethanol. The data in Table 1 are at higher %E or %A where other, probably mixed, reactive species may prevail and which might not respond to a change in %A or %E in the same way.[24]

IMPORTANCE OF ACTIVITY COEFFICIENTS AND THEIR PREVIOUS USE IN SOLVOLYSIS REACTIONS

We believe that in addition to Symons' concepts, the change in the solvent interactions affecting the kinetic activity coefficients of ethanol and water (KAC_E, KAC_W) when the solvent is changed must be considered and might help answer the questions posed above. By 'kinetic activity coefficients' we mean those terms which should multiply the molarities of E and W in equation (1) in order to obtain 'solvent-free' selectivities. KAC_E and KAC_W cannot be measured independently, but the interactions affecting the *KAC*s (i.e. dipole–dipole interactions, hydrogen bonding, dispersion forces and structure making or breaking[26]) are also reflected in the partial vapour pressures of the solvent components, and the Raoult's law activity coefficients of E and W (γ_E and γ_W) calculated from them.[27] Therefore, changes in KAC_E and KAC_W could be deduced from changes in γ_E and γ_W.

Ingold and co-workers[9,28] preferred the use of partial pressures of W and E rather than their concentrations in studying the solvolysis of butyl halides in E–W mixtures. Following Olson and Halford,[29] they regarded the transition state as a mode of 'escape,' so that the tendency for its formation should be correlated with fugacity (or activity) measures. Nevertheless, activity coefficients were usually not used in LFER investigations of solvolysis reactions, except in the work of Luton and Whiting,[21] who investigated the solvolysis of several 1-adamantyl derivatives in 50–95% E–W. The k_E/k_W values changed very little for the bromide, but for the picrate and 2,4-dinitrophenolate, and especially for the tosylate, they decreased significantly on increasing the concentration of E (*ca* 30% in 50–95% E–W). They observed 'a good linear relationship' between the k_W/k_E values and the activity coefficient ratio γ_W/γ_E with slopes ranging from 0·1 for the bromide to 0·6 for the tosylate. The values of the slopes were taken as measuring 'the need during the formation of the solvent-separated ion pair to isolate the interstitial solvent molecule from the rest of the solvent.'

Blandamer *et al.*[30] noticed that in E–W, $\Delta G^{\ddagger}$ for *t*-BuCl solvolysis decreased when the positive excess molar Gibbs function of mixing, G^E, decreased. This was ascribed to a more hydrophilic transition state than the ground state. The G^E function is directly connected to γ_E and γ_W, but this point was not investigated further.

Parker[26] related the ratio of the rate constant for a bimolecular reaction of an anion Y^- with RX in a solvent, S, and in a reference solvent, O, to the appropriate solvent activity coefficients:

$$\log(k^S/k^O) = \log{}^O\,\gamma^S_{Y^-} + \log{}^O\,\gamma^S_{RX} - \log{}^O\,\gamma^S_{YRX^{\ddagger}} \quad (2)$$

He regarded bimolecular solvolysis reactions as unsuitable for this treatment because solvolysis in two different solvents 'is a bimolecular reaction with two different reagents.'

We note that the last problem does not apply when measuring selectivity values at different E–W compositions. Further, if E and W react with the same intermediate, the k_E/k_W values should be relatively independent of its γ and of the γ of the transition state, as the species involved are relatively large and similar. Consequently, the selectivity changes, regardless of the system, should mainly reflect changes in the γ_E/γ_W ratio, in line with the data in Table 1.

CONTRIBUTION OF ACTIVITY COEFFICIENTS TO THE SELECTIVITY

Several activity coefficients γ_E and γ_W in binary E–W, A–W and E–A mixtures at 40 or 45 °C were calculated from vapour pressures given in the literature[31,32] by regular procedures[27] and are displayed in Table 2. A literature search revealed that the γ values are almost insensitive to the temperature in the region of interest (see footnotes to Table 2). In each binary system the γ value of each component changes regularly on changing its relative concentration and values at three representative volume percentages are given. At very low concentrations of each component in a binary mixture the γ values tend to change sharply, thus rendering them very sensitive to experimental errors. However, for our concentration range, different literature sources give very similar values for E–W.[31,33,34]

The effects of E or A on γ_W and of A on γ_E are all moderate and very similar, but the effect of W on γ_E is twice as large in the same solvent range (Table 2). It therefore seems reasonable that when A is added to an

E–W mixture with a fixed composition, and the medium surrounding each nucleophile contains more A and less E and W, the main effect will be lowering of γ_E and therefore also lowering of k_E/k_W.

Table 2. Influence of the cosolvent B on γ_A in EtOH–H_2O, Me_2CO–H_2O and Me_2CO–EtOH mixtures at 40 °C

A	B	[B]/% v/v	γ_A	γ_A^h/γ_A^l [a]
H_2O[b]	EtOH	24	0·96	
		46	1·06	1·5
		75	1·43	
H_2O[c]	Me_2CO	24	1·06	
		46	1·20	1·35
		75	1·43	
EtOH[b]	H_2O	25	1·29	
		46	2·25	2·8
		76	3·64	
EtOH[d]	Me_2CO	24	1·05	
		46	1·17	1·4
		75	1·46	

[a] Ratio of activity coefficients at highest (γ_A^h) and lowest (γ_A^l) B concentrations.

[b] The γ values were calculated from partial pressures given in Ref. 31 and they do not change significantly between 20 and 75 °C. The estimated error is $\leq \pm 0\cdot5\%$.

[c] γ Values at 45 °C were calculated from partial pressures given in Ref. 31. They change slightly and irregularly with temperature in the range 25–60 °C. The estimated error is ±6%.

[d] γ Values were calculated from total pressures and molar fractions of acetone in liquid and gas phases given in Ref. 32. γ_E decreases by <6% between 32 and 48 °C. The estimated error is <0·5%.

In an attempt to obtain a clearer and more quantitative evaluation of the effect of the change of the medium, we tried to compare k_E/k_W values in solvent mixtures which differed only in the volume percentage of one nucleophilic component. For example, in the solvolysis of Ph_2CHCl at 25 °C[11] in 30:30:40 W–E–A, $k_E/k_W = 3\cdot24$; in 30:70 W–E, $k_E/k_W = 3\cdot25$; and in 70:30 W–E, $k_E/k_W = 4\cdot50$. The last value was extrapolated from results at higher ethanol concentrations using the linear k_E/k_W vs Y plot.[11]

Similar comparisons were obtained for other combinations of the three solvents and for other systems. The results are represented graphically in Figure 1 for the diphenylmethyl, octyl, 1- and 2-adamantyl systems. $PhCH_2Cl$ behaves very similarly to $C_8H_{17}Br$. Almost all the points at high water concentrations (lines W in Figure 1) are extrapolated from experimental values at lower water concentrations using the mY relationship for diphenylmethyl[11] and octyl halides and a log k_E/k_W vs %E plot for 1- and 2-adamantyl derivatives.[14] Hence, lines W should be viewed as reflecting only an estimate of the true behaviour of these systems at high water volume percentage, but our qualitative conclusions remain valid. It may be argued that the effect of the medium on the selectivity values should be analysed by comparing solvent mixtures with fixed molar fractions of ethanol or water rather than fixed volume percentages. However, both are important in determining the activity of each component in a mixture[35] and we also found that comparisons based on molar fractions gave very similar plots to those here. It is immediately discernible from Figure 1 that substituting A for E lowers the selectivity values much less than substituting A for W. The overlap of the A and E lines for Ph_2CHCl in Figure 1(4), which reflects nearly identical k_E/k_W values in E–W and E–W–A mixtures having identical percentages of water is probably fortuitous.

We suggest that although the behaviour represented

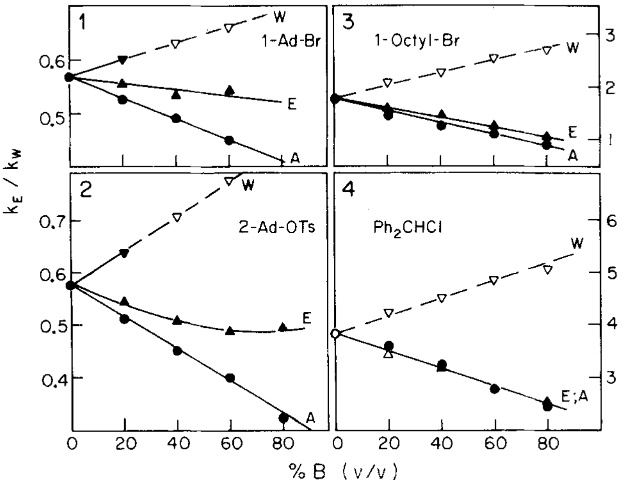

Figure 1. Medium effects on selectivity values in (1) 1-Ad-Br, (2) 2-Ad-OTs, (3) 1-octyl-Br and (4) Ph_2CHCl. Solutions were prepared using X% of B and (100 − X)% of 60% E–W (in 1 and 2) or 50% E–W (in 3 and 4). B represents A, E or W. Full symbols represent measured or interpolated values, open symbols represent extrapolated values (see text)

in Figure 1 results mainly from changes in the kinetic activity coefficients as reflected in the change in γ_E and γ_W (Table 2), it is also affected by the action of A or E as basic cosolvents according to Symons' proposals. Each of these two factors is insufficient alone to account for all the changes observed. Unfortunately, a real quantitative evaluation of the contribution of the changes of the γ values to the selectivity values is hindered by the lack of data on these γ values in the ternary system W–E–A. A method to calculate γ values in a multicomponent solution using a combination of parameters derived from data for binary mixtures is available.[35] Since the method is very cumbersome and gives only approximate results, we did not apply it to calculate γ values in W–E–A mixtures, but qualitative speculations concerning the ternary mixture, on the basis of the γ values for the separate binary mixtures, are justified. A simplified approximation is to regard each γ in W–E–A mixtures as a simple average of those in the binary mixtures (i.e. γ_E in 30:30:40 W–E–A is the average of γ_E in 50:50 W–E and in 43:57 E–A). Using such approximation and γ values calculated from the literature,[31,32] we estimate that a change from 70:30 W–E to 30:30:40 W–E–A will lower γ_E/γ_W by a 2·3-fold, which is more than the actual largest observed decrease in k_E/k_W values for this solvent change [1·8-fold decrease for *n*-octyl bromide; cf. Figure 1(3)]. A change from 30:70 W–E to 30:30:40 W–E–A will increase γ_E/γ_W by 35% whereas the observed k_E/k_W values remain unchanged or decrease by up to 10%.

This last discrepancy, which is even larger at higher %A and is especially marked for the 1- and 2-adamantyl systems, can be ascribed to the aforementioned action of acetone as an OH_f scavenger and therefore an LP_f 'producer' for both E and W, and the similar such effect of E on W. It can be deduced from Symons' work[24] that A, having a base strength comparable to that of dioxane, is slightly more effective than E and binds between one and two OH_f units per molecule, whereas E binds only one extra OH_f. Assuming that A and E act basically in the same manner even when their concentrations in the aqueous solution are high and OH_f and LP_f are probably replaced by mixed reactive species, we might speculate that these additional factors are responsible for the decrease, or lack of change, in the k_E/k_W values when A is substituted for E. Acetone binds and 'deactivates' a great part of the free hydroxyl groups that are present on E molecules in E–W (6% at 75 °C in pure ethanol[36]) and therefore lowers k_E for the adamantyl carbocations significantly, whereas the net effect on water, for which A replaces E, is much smaller. Consequently, the k_E/k_W ratios decrease. Lone pairs are important in the solvolysis of Ph_2CHCl and $C_8H_{17}Br$, and since the small increase in LP_f, caused by replacing part of the E with A, is kinetically important for W but not for E (lone pairs are present on either free or bonded E molecules), the k_E/k_W values will tend to decrease slightly. This effect will compensate the expected increase in k_E/k_W due to the change in activity coefficients (on substituting A for W the same line of reasoning suggests, at most, a small decrease in k_E/k_W for all the systems concerned; this may contribute to the marked decrease related above to the changes in the activity coefficients).

The relative insensitivity of the k_E/k_W values for 1-adamantyl-Br and 2-adamantyl-OTs to the E content in binary E–W mixtures[14] can also result from two opposing effects. An increase in E content means both higher γ_W/γ_E ratio (Table 2), and diminished W electrophilicity (OH_f units). In the other systems in Table 1, the nucleophilicity (LP_f units) of the solvent molecule is important and these two effects lead now to a total sharper decrease in k_E/k_W values (Luton and Whiting's selectivity values for 1-adamantyl 2,4-dinitrophenolate, picrate and tosylate[21] are inconsistent with the explanation of opposing effects of ethanol which is based on Karton and Pross's results[14] for 1-adamantyl-Br and 2-adamantyl-OTs. This might be due to different sensitivities of the different nucleofuges to the activities changes.[21] However, Luton and Whiting's correlations included only four data points and their actual values for 1-adamantyl-Br and tosylate do not differ by more than three times the estimated standard error. Moreover, Karton and Pross found almost identical k_E/k_W values for 2-adamantyl-Br and tosylate,[14] which were almost insensitive to E–W composition. Clearly, more data should be gathered before we can draw conclusions regarding the role of the nucleofuge).

The substantial dependence of k_E/k_W values on γ is consistent with their relative insensitivity to significant temperature changes between 25 and 120 °C.[7,10,11,13,21,37] That the γ values do not change significantly between 25 and 75 °C[31] is probably due to compensating effects of the temperature on the thermodynamic excess functions ΔH and ΔS.[38]

We note that McLennan and Martin's[10] results on the effect of added A on the solvolysis of the diphenylmethyl systems in E–W partially contradict those of Pross and Karton.[11] The main difference is the remarkable increase in the k_E/k_W values for $Ph_2CHOPNB$ (OPNB = *p*-nitrobenzoate) from 2·25 and 3·79 in 20:80 and 50:50 W–E, respectively, to 2·67 in 10:40:50 and to 6·61 in 25:25:50 W–E–A. Solvolysis of the diazo compound Ph_2CN_2 showed a similar increase only in 10:40:50 W–E–A, whereas in 25:25:50 W–E–A the selectivity value of 3·50 is lower than the value of 4·24 in 50:50 W–E. The different behaviour of $Ph_2CHOPNB$ and $Ph_2CN_2{}^+HOPNB$ was ascribed to different 'initial state solvation requirements,' which are especially important in the water-rich solutions where the discrepancy between the selectivity values for the two systems, with or without added acetone, is the largest. This suggestion raises some problems (for example, the authors stated that the solvolytic products from Ph_2CN_2 are not formed either from the diazonium ion pair $Ph_2CHN_2{}^+OPNB^-$ or from the intimate ion pair $Ph_2CH^+OPNB^-$ which is already common to both substrates[10]), and we also note that it is unclear why the solvolyses of Ph_2CHCl[11] and $Ph_2CHOPNB$[10] respond so differently to added A when their responses to changing E–W ratios are so similar.[10]

CONCLUSION

We believe that kinetic activity coefficients as modelled by γ values from partial vapour pressures play a major role in determining the selectivity values and their changes with the solvent in E–W mixtures, as well as in other binary solvent mixtures such as $MeOH-H_2O$ and $CF_3CH_2OH-H_2O$. For 1-adamantyl-Br in several solvent mixtures composed of two nucleophiles A and B, McManus and Zutaut[18] observed a tendency for the selectivity values k_A/k_B to decrease when the concentration of A increases. We are currently trying to determine the generality and scope of the above phenomenon and the factors that affect it in various substrate and solvent systems, since changes in the selectivity values are as informative as the values themselves in mechanistic studies.

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