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Preferential Solvation and Statistical Analysis for Solvent Polarity Parameters in MeOH Binary Mixtures

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Preferential solvation (PS) phenomena of solutes based on solvent polarity, E_T and AN, were studied by UV/vis. and NMR spectra in MeOH binary mixtures. According to the extent of solvent-solvent interaction, different solvation phenomena were found. PS concept was applied to explain the reactivity of *tert*-butyl halides solvolysis. The findings of solvation phenomena have been related to the rate of solvolysis and PS suggested as a reason for the solvent dependence of the rates of reaction. Moreover, we found that the results of prinicipal components analysis using six parameters are in good accordance with the results of PS phenomena in mixed methanol systems.

Introduction

Although the effect of solvent on the rate and the position of equilibrium of chemical reactions has been known for over a hundred year,[1] there are still no reliable and exact methods for a quantitative description and prediction of such solvent effects. But one of the most important selection criteria in this connection is a property of solvents generally known as 'solvent polarity'. Various empirical solvent polarity parameters have been often used effectively to describe the influence of solvents on physicochemical solute properties of different kinds[2,3] and there have been several attempts to correlate with the solvation phenomena of empirical or experimental parameters of solvent polarity and kinetic data in mixed binary solvents.[4-7]

In this work, we have studied solvation phenomena of solvent polarity (E_T[8] and AN[9]) in eight methanol mixtures since mixed binary solvents are extremely versatile and useful solvent systems, particularly in kinetic and spectroscopic studies. However, there have often been abnormal problems in kinetic and spectroscopic studies in mixed solvent systems. One of those involves the possibility of PS. This implies that the difference in the specificities of interaction of solute with the component solvents, the composition of the solvents in the immediate vicinity of the solute may be different from that in the bulk. It is obvious that PS may be of paramount importance in the interpretation of spectroscopic and kinetic data obtained in binary systems.[10-14] In this reason, the reactivity of *tert*-butyl halides solvolysis has been discussed by comparing PS phenomena of polar solutes based on solvent polarity in methanol mixtures.

And that the classification of mixed binary solvents is proposed by treating a basis set of six solvent parameters (the Reichardt's E_T, solvatochromic parameters (π^*, α, β)[15,16] of Kamlet-Taft and Gutmann's AN, DN[17,18]) by the principal components analysis.[19,20] This classification is based on the representation of 41 mixed methanol solvents as points in a two-dimensional space, solvent similarity being measured from the distance between two points within this space.

Experimental

Materials. The solvents used were methanol (MeOH), dimethylsulfoxide (DMSO), pyridine (PY), dimethylformamide (DMF), methylcyanide (MeCN), dioxane, acetone (AC), 1,2-dichloroethane (DCE) 1,1,2,2-tetrachloroethane (TCE), *n*-hexane and carbon tetrachloride. All of the solvents were spectrophotometric grade of Aldrich Chemicals and each solvent was dried over molecular sieve 4 Å. Binary solvent mixture use were MeOH-DMSO, MeOH-PY, MeOH-DMF, MeOH-MeCN, MeOH-dioxane, MeOH-AC, MeOH-DCE and MeOH-TCE and prepared by weight at nominally round mole fraction with intervals of 0.1.

AN indicator, triethylphosphine oxide (Et$_3$PO) was pur-

chased from Alpha Chemical Co. and diphenylphosphinic chloride [$(C_6H_5)_2POCl$] and methanol-d(MeOD) were NMR grade of Aldrich Chemicals. E_T indicator, 2,6-diphenyl-4-(2,4, 6-triphenyl-1-pyridinum)-1-phenolate was a gift from Prof. C. Reichardt, Marburg (FRG). DN indicator, [(N,N,N',N'-tetramethylethylenediamino)-acetylacetonato] copper(II) perchlorate was prepared from copper(II) perchlorate hexahydrate, 2,4-pentadione and N,N,N',N'-tetramethylethylenediamine by neutralization, partial evaporation of the solvent, and recrystallization.[21]

Method. UV spectral measurements were made in 1 cm light path quartz cells with a Kontron Uvicon 860 spectrophotometer at the controlled temperature of 25.0 ± 0.2℃. The concentration of the indicators was about 10^{-4}-10^{-5} mol·dm^{-3}. The accuracy of the assignment of the wavelength of the maximum absorption was in the range of ± 1 nm. ^{31}P-NMR chemical shifts were measured by Bruker 500 MHz superconducting spectrometer. Sample tubes were 10 mm Bruker glass tube with coaxial inner cells filled with $(C_6H_5)_2POCl$ as external reference. External locking material was MeOD. For each solvent chemical shifts were determined for three different concentrations, usually in the range 0.4 to 0.05 mole Et$_3$PO/liter.

All ^{31}P spectra were recorded with proton decoupling in order to obtain a maximum in accuracy sensitivity. The chemical shift values determined were corrected for difference in bulk diamagnetic susceptibility between sample and reference according to the relationship of Live and Chan for high-field spectrometers.[22]

The hydrogen bonding formation constants were measured as the method of ref 23 using Nicolet 250 FT-IR spectrophotometer.

Statistical Analysis Methods

41 mixed methanol systems were selected to provide a range of each of six basis variable. Six basis variable, E_T, AN, DN, π^*, α and β are solvent effect parameters. The six basis variables define a six-dimensional space in which every mixture may be represented as a point. Principal components analysis has been calculated by a correlation method because among variables there exists some good correlations.

Principal components analysis uses linear combinations of basis parameters to replace the starting set of n basis variables (here $n = 6$) by another set of p orthogonal principal components ($p \leq n$). Every principal component is a linear combination of the starting variables, and the new set is built in such a way that each principal component bears in turn the maximum of variance. A geometrical analogy may classify this process: the first principal component is directed along the principal axis of the ellipsoid defined by the cloud of points (in the six-dimensional space initially defined). The other principal components are then built from the first one by applying the orthogonality condition within the n-dimensional space. This process of orthogonalization aims to replace the starting set of more or less correlated variables by a new set of fully independent variables. Furthermore, there is a quantified hierarchy in the information content of the variable space: the principal component plays a determining role in the description of the whole population of individuals: the last principal component plays the least sig-

nificant role; suppression of the least significant principal component may cause no important distortion in the description of the population. The distortion incurred by component suppression may be expressed as a percentage of information lost. As a consequence, it is possible to pass from a n-dimensional space to a simpler p space by the successive removal of n-p components, and at each removal the loss of information is quantitatively assessed.

Results and Discussion

Solvation of E_T and AN. The results of E_T and AN values for each mixed solvents are shown in Figure 1. Although these values are not simple correlation with composition of the solvent mixture, we hope to detect some general trends of changes in the solvent polarity dependending on the composition of the mixture. If the solvation of solutes by the components of a binary solvent mixture is random, i.e., non-specific, then one would expect a linear relationship between polarity values of the mixture and mole fraction, i.e.,

$$E_T = E_T°_{(1)}X_1 + E_T°_{(2)}X_2$$
and
$$AN = AN°_{(1)}X_1 + AN°_{(2)}X_2 \tag{1}$$

where $E_T°_{(1)}$, $E_T°_{(2)}$, $AN°_{(1)}$, and $AN°_{(2)}$ are the values for the pure liquids and X_1 and X_2 represent the mole fraction of the component solvents in the mixture.

But, we can see that the Figure 1 is non-linear. It is likely to arise from PS of the solutes by the mixture. In mixed solvents, the non-linear behavior of some properties of a solute as a function of solvent mole fraction has been used on a number of occasions to make deductions concerning solvation. A convenient method of representing the departure from a linear relationship of polarity values is by making of the concept of an excess function, such that

$$E_T = E_T°_{(1)}X_1 + E_T°_{(2)}X_2 + \Delta E_T$$
and
$$AN = AN°_{(1)}X_1 + AN°_{(2)}X_2 + \Delta AN \tag{2}$$

ΔE_T and ΔAN values were calculted for each of the solvent mixtures. The values of deviation for all the systems studied are given in Table 1 and the positive deviation values represent PS of the solute by methanol.

The solvent mixtures given in Figure 1 and Table 1 can be divided into three groups from the different solvation of solute. The first group of solvent mixtures seems to exhibit weak PS phenomena for the solute due to the strong sovent-solvent interaction (e.g., MeOH-DMSO, MeOH-PY and MeOH-DMF). In these mixtures, deviations are relatively small because the correlation between solvent polarity and solvent composition is close to linearity ($\Delta E_T \leq 3$, $\Delta AN < 2.0$ at $X_{MeOH} = 0.5$). The second group of solvent mixtures show the strong PS of the polar solutes (e.g. MeOH-MeCN, MeOH-Dioxane and MeOH-AC). This group has large positive deviations due to the strong solute-solvent interaction with the strong solvation of solute by the more polar methanol. It is interesting to show the maximum E_T for MeOH-MeCN mixture at a methanol mole fraction of ca. 0.9 in MeOH-MeCN mixture. Similar measurements for Kamlet-Taft's solvatochromic parameters of MeOH-MeCN binary mixture have been
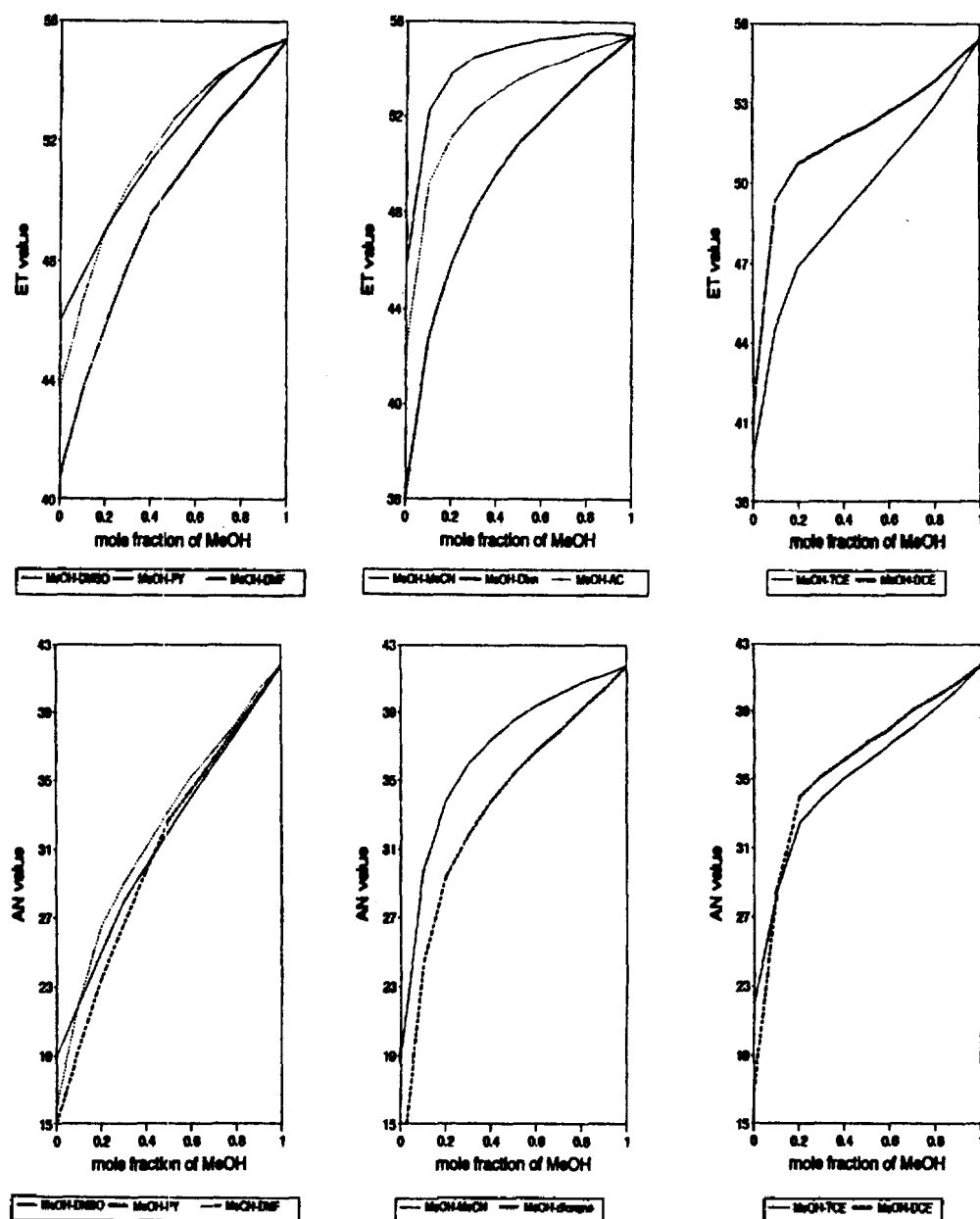
Figure 1. Plots of E_T and AN vs. mole fraction of MeOH for the mixed methanol solvents.

carried out by Lee *et al.*[6]

This result also exhibited a maximum $\pi^*+\alpha$ at ~0.9 MeOH. We assume that this maxium phenomenon might be origin from the cooperative behavior between methanol and HBD acidity ability of MeCN. We can see that these two results are well consistent with each other. In the cases of MeOH-DCE and MeOH-TCE mixtures, the changes of E_T and AN seem to have a very weak solvent-solvent interaction, *i.e.*, in the region of $0.2<X_{MeOH}<1.0$ polarity change is a little, whereas in $X_{MeOH}<0.2$ polarity change is steeply decreased to pure DCE and TCE.

The extent of solvation of a solute in MeOH mixtures mainly depends on not only solute-solvent interaction but solvent-solvent interaction. A more equitable estimate of the extent of solvent-solvent interaction can be judged from the hydrogen bonding between MeOH and dipolar aprotic sol-

vent.

In this work, the formation constant (K_f) is determined for the hydrogen-bonded-complexes between MeOH and six basic solvents. Table 2 shows that the K_f values of first group (MeOH-DMSO, MeOH-PY and MeOH-DMF) are higher than those of second group (MeOH-MeCN, MeOH-dioxane, and MeOH-AC). The high K_f values generally represent strong hydrogen bonding between solvent molecules.

It has been known that the PS plays an important role of reaction rates in mixed solvents. Recently, Koppel demonstrated a correlation between the change of E_T values and reactivity of *tert*-cumyl chloride,[24] and the correlation was also investigated between the PS of pyridinium betaine and some kinetic studies of solvolysis in mixed solvent systems by Dawber *et al.*[5]

It is well-known that the solvolyses of *tert*-butyl halides

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Table 1. ΔE_T and ΔAN Values in MeOH Binary Mixtures at Various Mole Fraction

Cosolvent	ΔE_T/kcal·mol^{-1}								
X_{MeOH}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
DMSO	1.30	1.78	1.96	2.06	1.98	1.88	1.71	1.36	0.76
PY	1.85	2.11	2.72	2.91	2.53	2.11	1.64	1.02	0.47
DMF	1.77	3.90	3.29	3.26	3.17	2.78	2.32	1.61	0.86
MeCN	5.78	6.05	5.76	5.11	4.42	3.68	2.83	1.97	1.07
Dioxane	4.77	5.68	6.00	5.69	4.98	4.01	2.94	2.04	1.03
AC	5.72	6.33	6.13	5.53	4.80	3.94	2.92	1.91	1.11
TCE	3.31	3.70	3.32	2.51	2.11	1.06	0.88	0.39	0.06
DCE	6.49	6.44	5.58	4.60	3.57	2.61	1.09	1.09	0.61
Cosolvent	ΔAN								
X_{MeOH}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
DMSO	1.69	1.59	1.49	1.42	1.30	1.25	1.19	1.16	1.14
PY	1.84	1.91	1.85	1.83	1.71	1.71	1.69	1.55	1.52
DMF	3.64	2.85	2.35	2.06	1.92	1.88	1.76	2.28	1.87
MeCN	10.23	7.70	7.00	6.61	6.09	5.62	5.21	4.85	4.52
Dioxane	6.82	5.80	4.82	4.34	3.81	3.45	2.97	2.76	2.25
TCE	3.95	4.39	3.54	2.96	2.51	2.17	1.90	1.62	1.41
DCE	7.95	6.23	5.60	5.38	5.02	4.46	4.13	4.06	3.16

Table 2. Formation Constant (K_f) for Hydrogen Bonding of MeOH to DMSO, PY, DMF, MeCN, Dioxane and AC in CCl₄ ($[A_o] = 0.025$ M, $1/\varepsilon = 2.99 \times 10^{-2}$)

Conc. of DMSO, $[B_o]$	0.010	0.025	0.040	0.060
Absorbance	0.703	0.550	0.442	0.344
$[A] \times 10^2$ M	2.102	1.645	1.322	1.029
$[C] \times 10^2$ M	0.398	0.855	1.178	1.471
K_f, M^{-1}	31.452	31.596	31.576	31.564
	K_f average = 31.5 ± 0.9 M^{-1}			
Conc. of PY, $[B_o]$	0.010	0.025	0.040	0.060
Absorbance	0.688	0.522	0.379	0.275
$[A] \times 10^2$ M	2.058	1.562	1.134	0.821
$[C] \times 10^2$ M	0.442	0.938	1.366	1.679
K_f, M^{-1}	38.489	38.445	38.436	38.434
	K_f average = 38.4 ± 1.0 M^{-1}			
Conc. of DMF, $[B_o]$	0.010	0.025	0.040	0.060
Absorbance	0.726	0.596	0.499	0.405
$[A] \times 10^2$ M	2.171	1.782	1.492	1.211
$[C] \times 10^2$ M	0.329	0.718	1.008	1.289
K_f, M^{-1}	22.352	22.610	22.580	22.594
	K_f average = 22.5 ± 0.7 M^{-1}			
Conc. of MeCN, $[B_o]$	0.010	0.025	0.040	0.060
Absorbance	0.794	0.736	0.687	0.629
$[A] \times 10^2$ M	2.374	2.201	2.054	1.881
$[C] \times 10^2$ M	0.126	0.299	0.446	0.619
K_f, M^{-1}	6.073	6.172	6.110	6.116
	K_f average = 6.12 ± 0.06 M^{-1}			
Conc. of dioxane, $[B_o]$	0.010	0.025	0.040	0.060
Absorbance	0.784	0.715	0.658	0.592
$[A] \times 10^2$ M	2.344	2.138	1.967	1.77
$[C] \times 10^2$ M	0.156	0.362	0.533	0.730
K_f, M^{-1}	7.885	7.919	7.816	7.826
	K_f average = 7.86 ± 0.04 M^{-1}			
Conc. of AC, $[B_o]$	0.010	0.025	0.040	0.060
Absorbance	0.782	0.710	0.650	0.582
$[A] \times 10^2$ M	2.338	2.213	1.944	1.740
$[C] \times 10^2$ M	0.162	0.377	0.556	0.760
K_f, M^{-1}	8.268	8.365	8.305	8.336
	K_f average = 8.32 ± 0.08 M^{-1}			

are faster in protic solvents than in dipolar aprotic solvents because of the stabilization of the leaving group anion through hydrogen bonding.[3] Figure 2 shows such a plot for *tert*-butyl halides in eight different solvent mixtures where some deviation from linearity in rate behaviour with solvent mole fraction is observed. The direction of non-linearity would suggest PS of the substrate mainly by methanol and that these phenomena are greater in second group (Figure 2 (d), (e), (f)) than in first group (Figure 2 (a), (b), (c)). Thus, although the rate constants for the solvolysis of *tert*-butyl halides are not known at lower methanol concentration in MeOH-DCE and MeOH-TCE mixture, these are similarly behaviour as the change of E_T and AN.

However, according to the extents of solvent-solvent interaction and leaving ability of halides appear the differencies of the solvation of solutes by MeOH in mixtures. In the cases of DMSO, PY and DMF mixtures, it is seen that the PS is not primarily associated with the halogen leaving group in the reaction. Strangely, the solvolysis rate of *tert*-butyl iodide increases from MeOH to DMSO. Mishuhashi[25] demonstrated that the quantity, $P = RT\ln(k_{DMSO}/k_{MeOH})$ (kcal/mol) may serve as a measure of the relative importance of ionizing power between dipolar aprotic and protic solvents in polar unimolecular reactants. He regards this reaction as "hydrogen-bond-insusceptible" which lacks the ability to strengthen hydrogen bonding with protic solvents during charge separation, giving a positives PS values ($p > 1$). In this regard, it is an acceleration not due to the hydrogen bonding, but to the elimination behavior of solute.

However, ths second group shows that specific solvation of halide anions with MeOH is an important factor in the rate of reaction. In MeOH-TCE and MeOH-DCE mixtures, the reaction of the *tert*-butyl halids is entirely dependent on the magnitude of solvation of halide anions by MeOH

because of negligible or very weak solvent-solvent interaction. From Figure 1 and 2, we have seen that the rate constants of *tert*-butyl halides in mixed methanol solvents correlate with PS phenomena of polar solutes, *i.e.*, E_T and AN.

Statistical Analysis. A classification procedure for MeOH mixture systems is proposed by treating a basis set of six solvent polarity variable of the multivariate statistical method (Table 3).

We have made use of the Kamlet-Taft's parameters in previous works.[6,7,28] The eigenvalues, percentage of total variance with each eigenvector and cumulative percentage of
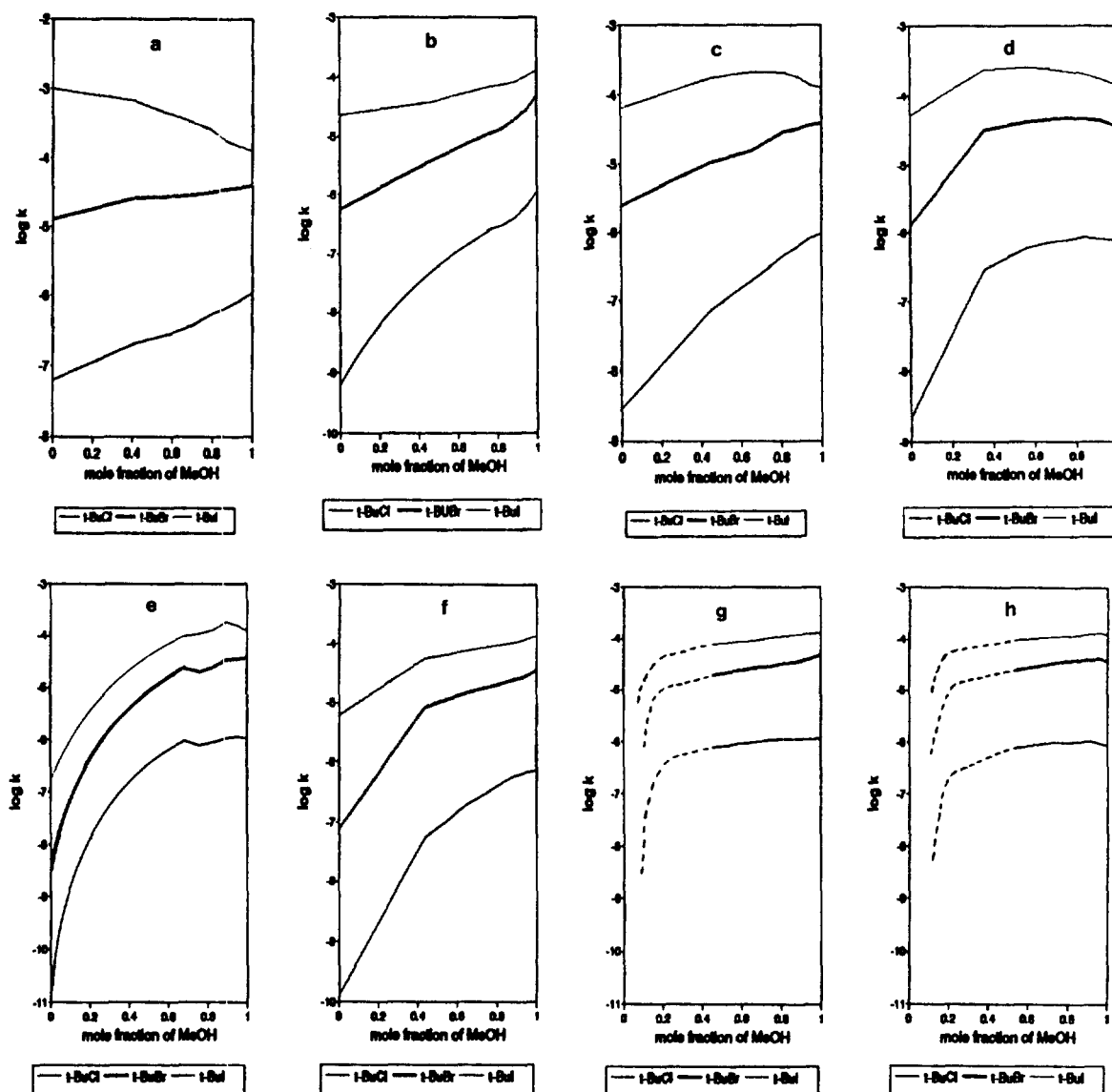
Figure 2. Plots of log k for the solvolysis of *tert*-butyl halides *vs.* mole fraction of MeOH: (a) MeOH-DMSO, (b) MeOH-PY, (c) MeOH-DMF, (d) MeOH-MeCN, (e) MeOH-dioxane, (f) MeOH-AC, (g) MeOH-DCE and (H) MeOH-TCE mixtures. [1]Rate constants of pure DMSO and PY are calculated from data at other temperature in ref 25 and ref 26. [2]Rate constants of pure DMF, MeCN, dioxane, and AC obtained from ref 27. [3]Although the solvolysis of *tert*-butyl halides in pure DCE and TCE is not occurred, dotted lines are imaginary values.

variance are given in Table 4. The sum of first principal component (PC1) and second principal component (PC2) occupied with 86.7% of the total variance. As a consequence, the suppression of the four least significant principal components entrains a loss of only 13% of the total information.

The eigenvector coefficient corresponding to each eigenvalue and the communalities of the variable in each of the derived eigenvectors, *i.e.*, the fraction of total variance accounted for in each component, are given in Table 5 to show the importance of given variable in an eigenvector. The table also shows that the PC1 is strongly correlated with acceptor number, π^*, α and E_T. PC1 mainly contains therefore the property of Lewis acidity of the solvent. The PC2 is well correlated with β and DN. Therefore, it is the representative of the Lewis basicity of solvent.

However, the PC1 has the greatest proportion of the total information. This indicates that Lewis acidity of the solvent is the most important factor to the relative positions of mixture.

Figure 3 is the presentation of the mixture systems in the plane of PC1 and PC2. The plot shows that the points of the mixed solvent form three distinct groups, *i.e.*, square points are the mixtures of highly solvent-solvent interaction such as MeOH-DMSO and MeOH-PY, triangle points are the mixtures of negligible solvent-solvent interaction such as MeOH-DCE and MeOH-TCE. Circle points are the MeOH-MeCN and MeOH-dioxane mixtures which has the middle intensity of solvent interactions of square group and triangle group. These results of classification from principal component analysis are in good accordance with the results

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Table 3. Parameter Data of 41 Mixed Solvent Systems Used in the PCA

Parameter Sample No.	E_T	DN	AN	π^*	α	β
1	55.41	19.00	41.74	0.586	0.980	0.620
2	55.30	22.60	40.57	0.652	0.704	0.641
3	54.98	23.73	39.27	0.701	0.549	0.627
4	54.71	26.43	37.76	0.756	0.297	0.641
5	54.15	27.33	35.95	0.793	0.204	0.660
6	53.34	28.45	34.23	0.826	0.184	0.702
7	51.42	29.13	30.07	0.893	0.079	0.737
8	55.41	19.00	41.74	0.600	0.977	0.600
9	55.52	18.80	41.24	0.680	0.801	0.595
10	55.52	18.59	41.13	0.730	0.721	0.572
11	55.41	17.37	40.44	0.772	0.621	0.572
12	55.35	16.76	39.83	0.816	0.504	0.538
13	55.20	16.35	39.15	0.816	0.490	0.538
14	54.67	15.73	37.12	0.854	0.343	0.519
15	55.41	19.00	41.74	0.586	0.980	0.620
16	54.72	19.00	41.12	0.592	0.957	0.560
17	54.25	19.00	40.45	0.629	0.850	0.488
18	53.24	18.85	39.80	0.688	0.735	0.390
19	52.65	18.70	39.06	0.716	0.639	0.379
20	51.84	18.70	38.24	0.742	0.580	0.372
21	49.38	18.50	36.41	0.847	0.324	0.246
22	55.41	19.00	41.74	0.600	0.980	0.617
23	54.93	19.00	41.43	0.630	0.831	0.574
24	54.51	19.90	40.77	0.651	0.804	0.518
25	53.79	18.57	40.45	0.686	0.736	0.460
26	53.49	18.57	39.86	0.712	0.722	0.408
27	52.75	18.35	39.01	0.749	0.560	0.375
28	51.80	18.13	37.21	0.792	0.377	0.124
29	55.41	19.00	41.74	0.600	0.980	0.620
30	54.88	19.95	40.91	0.756	0.496	0.622
31	54.30	20.89	39.99	0.784	0.416	0.623
32	53.84	21.71	38.21	0.799	0.368	0.627
33	53.04	23.75	0.00	0.811	0.291	0.629
34	52.36	24.96	35.66	0.820	0.116	0.631
35	50.16	28.36	30.88	0.845	0.009	0.634
36	55.41	19.00	41.74	0.578	0.980	0.619
37	54.83	18.79	40.85	0.616	0.871	0.608
38	54.46	18.58	40.26	0.631	0.804	0.606
39	53.95	18.37	39.63	0.638	0.635	0.617
40	53.09	18.16	38.75	0.654	0.536	0.605
41	52.41	17.53	37.70	0.663	0.435	0.588

Table 4. Eignevalues and Their Contributions

Component	1	2	3	4	5	6
Eigenvalue	146.92	61.28	20.14	7.60	2.46	1.60
Contribution (%)	61.2	25.5	8.4	3.2	1.0	0.7
Cumulative (%)	61.2	86.7	95.1	98.3	99.3	100

of the PS phenomena in former section. In this statistical analysis, we can predict not only classification of group but

Table 5. Eignevector Coefficient and Communalities

Parameter	Eigenvector Coefficient		Communalities	
	Comp. 1	Comp. 2	Comp. 1	Comp. 2
E_T	0.395	−0.393	22.922	9.464
DN	−0.367	−0.470	19.788	13.536
AN	0.504	0.039	37.319	0.093
π^*	−0.452	0.112	30.016	0.768
α	0.500	0.018	36.729	0.019
β	−0.006	−0.782	0.005	37.474
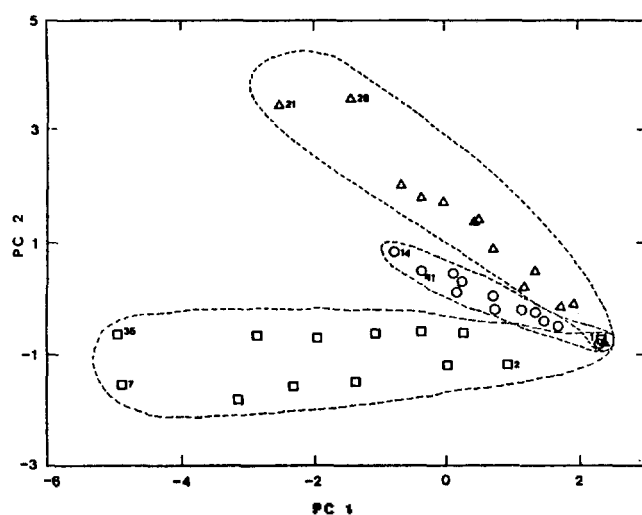
Figure 3. Plots of principal component 1 vs, principal component 2 for solvent mixture of Table 3 (□: MeOH-DMSO, MeOH-PY, ○: MeOH-MeCN, MeOH-dioxane, △: MeOH-DCE, MeOH-TCE).

the solvation ability of mixtures into classified groups.

Therefore, as expected from statistical calculation, it can be assumed that the MeOH-DMF and MeOH-AC mixtures are associated with square points group (MeOH-DMSO, MeOH-PY) and circle points group (MeOH-MeCN, MeOH-dioxane) respectively.

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The Effect of Solvent on the α-Effect(3): Nucleophilic Substitution Reactions of Aryl Acetates in MeCN-H₂O Mixtures of Varying Compositions

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Second-order rate constants have been measured spectrophotometrically for the reactions of substituted phenyl acetates with butane-2,3-dione monoximate and p-chlorophenoxide anions in MeCN-H₂O mixtures of varying compositions. The reaction rate, unexpectedly, decreased remarkably upon initial additions of MeCN to H₂O up to 30-40 mole % MeCN, and followed by a gradual increase upon further additions of MeCN. The change in solvent composition also influenced the magnitude of the α-effect, *i.e.*, the α-effect increased as the mole % MeCN increased. The solvent dependent α-effect for the present system appears to indicate that the differential solvation between the α-effect nucleophile and the corresponding normal nucleophile is not solely responsible but the difference in the transition-state stabilization is also responsible for the α-effect in organic solvent-rich region.

Introduction

Edwards and Pearson classified a group of nucleophiles which showed abnormally enhanced reactivity toward a variety of substrates relative to their basicity toward hydrogen.[1] A common feature of such nucleophiles is the possession of one or more unshared pairs of electrons adjacent to the nucleophilic center (the α-position). Thus, this enhanced reactivity has been termed α-effect[1] and nucleophiles exhibiting the α-effect include both uncharged nucleophiles such as hydrazines, hydroxylamine and methoxylamine and anionic ones such as peroxy anions, hypochlorite, oximates,

hydroxamates anions, etc.

Numerous studies have been performed to investigate the origin of the α-effect,[2] including (a) destabilization of the ground-state due to repulsion between nonbonding electron pairs;[3] (b) stabilization of the transition-state by overlap of the orbitals of the lone pair of electrons in the α-position;[1,4] (c) product stability,[5] (d) intramolecular general acid and base catalysis;[6] (e) polarizability;[1,7] (f) solvation effects.[8,9] However, any one of these effects alone does not fully account for the cause of the α-effect. Especially factor (f) has been the subject of controversy. It has been claimed that solvent effect is insignificant as the origin of the α-effect[8] but other studies,