Limitation of the ET(30) solvent strength scale in reversed-phase liquid chromatography

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Abstract

The transition energies (E_T) of the maximum absorption of the solvatochromic indicator denoted ET(33) [2,6-dichloro-4-(2,4,6-triphenyl-N-pyridino)-phenolate] in methanol–, acetonitrile–, isopropanol–and tetrahydrofuran–water mixtures over the full range in composition were measured. Its relationships with those for the closely related indicator ET(30) [2,6-diphenyl-(2,4,6-triphenyl-N-pyridino)-phenolate] were studied. Although the two indicators have very similar structures and hence we expected them to sense via their solvatochromic shifts the same intermolecular interactions exerted by the solvent in a similar way, plots of $E_T(33)$ vs. $E_T(30)$ are definitely non-linear. This and non-linearities in plots of ln k' vs. $E_T(30)$ and ln k' vs. $E_T(33)$ obviate the generality of a *single*-parameter solvent strength scale in RPLC.

1. Introduction

The "polarity" of the mobile phase is a major factor that influences solute retention in reversed-phase liquid chromatography (RPLC). For non-polar solutes retention in RPLC monotonically increases as the "polarity" of the mobile phase is increased upon addition of water. Many empirical scales of overall solvent strength and polarity have been proposed. These are typically based on either the effect of solvent on the rate of a chemical reaction or more commonly its influence on some spectroscopic property of a *single* indicator [1–10]. All the above-cited scales

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have been proposed as single-parameter overall scales of solvent strength. In contrast, the Kamlet–Taft multi-parameter π^*, α and β solvent scales [11–13] although highly empirical are based on the differential evaluation of solvent dipolarity/polarizability (π^*), solvent hydrogen bond (HB) donating acidity (α), and solvent HB accepting basicity (β). Although empirical the Kamlet–Taft scales have the advantage of being fundamentally interpretable. That is, π^* is decoupled from solvent hydrogen bonding processes and similarly solvent α and β are not related to solvent dipolarity. The $E_T(30)$ scale [14–16] and Kamlet–Taft multi-parameter scales [17–20] have both been used to study retention in RPLC. $E_T(30)$ has been used to correlate the effect of mobile phase composition on solute retention in RPLC [14–16]. Extrapolation of ln k' vs. $E_T(30)$ to 100% water has been proposed

as the basis of a universal method for estimating ln k'_w, the capacity factor using pure water as the eluent, for use in correlating octanol–water partition coefficients [21,22]. $E_T(30)$ measurements in mixed aqueous–organic media have been used to study the effect of media on organic reactions [23,24].

Comparison of structures I and II below shows that ET(33), 2,6-dichloro-4-(2,4,6-triphenyl-N-pyridino)-phenolate [25], has the same structure as ET(30), 2,6-diphenyl-(2,4,6-triphenyl-N-pyridino)-phenolate, except that the two phenyl groups at the 2,6-positions on the phenoxide ring are replaced by two chlorine atoms, which makes the pK_a of ET(33) (4.38) lower than that of ET(30) (8.65) [25].

ET(30)   ET(33)

I   II
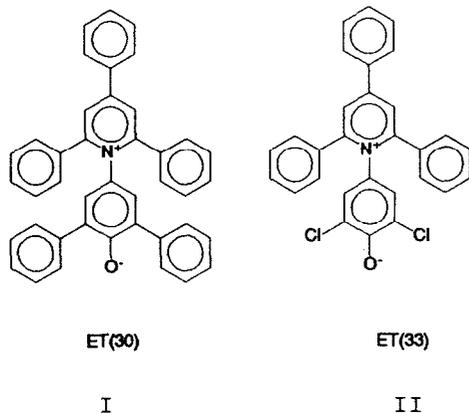
In addition the absorption maximum of ET(33) occurs at a shorter wavelength than ET(30) [25]. Since the structure of ET(33) is so very similar to that of ET(30) it should sense via its solvatochromic shift the same intermolecular interactions exerted by the solvent as does ET(30). Given this we expect that the transition energies (the so-called E_T value) of the maximum absorption for ET(33) should be linearly related to those for ET(30) in aqueous organic mixtures. In this work we measured the E_T values of the indicator ET(33) in methanol–, acetonitrile–, isopropanol–and tetrahydrofuran–water mixtures over the full composition range, and then examined the relationships between E_T values of ET(33) and ET(30) and relationships between RPLC ln k' and both $E_T(30)$ and $E_T(33)$ in these mixtures.

We observed that plots of $E_T(33)$ vs. $E_T(30)$ for the above four mixtures are non-linear and that plots of ln k' vs. $E_T(33)$ and vs. $E_T(30)$ are also non-linear when the full range of water–organic composition is considered.

The initial motivation for the present study was our concern that the greater pH sensitivity of the ET(30) dye in comparison to the analogous dichloro dye [ET(33)] could be the source of some experimental difficulties. Previously we noted [26] that a measurement of the hydrogen bond donor acidity of methanol–water mixtures based on $E_T(30)$ showed a minimum at intermediate compositions. This behavior was not observed with other hydro–organic mixtures [26] nor with a chemically distinct indicator [27]. Thus we felt that it might be due to a peculiar property of this indicator perhaps due to protonation of the phenoxide. Note that the chloro substituents weaken the Bronsted basicity of the phenoxide in ET(33) relative to that of the phenoxide in ET(30). Chloro groups are electron withdrawing whereas phenyl groups are electron donating thus the phenoxide group of ET(33) is a weaker Bronsted base than is the phenoxide group of ET(30). In the course of this work we discovered with surprise that plots of $E_T(33)$ vs. $E_T(30)$ are not linear as the mobile phase composition is varied even though both dyes are totally unprotonated under all conditions encountered in this study.

Johnson et al. [14] have shown that plots of ln k' vs. the mobile phases' $E_T(30)$ parameters are very often more linear than are plots of ln k' vs. volume fraction of organic modifier. These results were obtained with a large number of solutes, but did not encompass the entire range in mobile phase composition. Recently we have shown [28], based on the linear solvation energy relationship of Kamlet and Taft [13], that there can be no global single-parameter solvent polarity scale for RPLC except when the solute and solvent are incapable of forming hydrogen bonds and, in addition, the energy of cavity formation is either negligible compared to the strength of the solute–solvent interactions or is strictly proportional to the strength of such interactions. When relationships of ln k' were examined vs.

$E_T(30)$ for extended ranges of solvent composition, plots for such non-polar and non-hydrogen bonding solutes as alkylbenzenes were not linear and were not necessarily better than plots vs. volume fraction of organic modifier. Sometimes ln k' is more linear with volume fraction of organic modifier than with $E_T(30)$. Linearity in plots of ln k' vs. $E_T(30)$ was observed over a limited range in composition. We thus concluded that a single-parameter solvent strength scale may provide a set of plotting coordinates that linearizes the data for interpolation or other practical concerns, but one should avoid theoretical interpretation of the meaning of the regression coefficients. However, theoretical interpretation of the regression coefficients for plots of ln k' vs. $E_T(30)$ and extrapolation of the plot for ln k' vs. $E_T(30)$ for a limited range of mixture composition to 100% water have been reported [21,22,29]. Thus we felt that it is important to show the limitations of the linearity of ln k' vs. $E_T(30)$. This was done by examining relationships between RPLC ln k' values and a different solvent polarity scale based on the chemically similar indicator, ET(33), which is believed to sense via its solvatochromic shift the same intermolecular interactions exerted by the solvent in a similar fashion to ET(30).

2. Experimental

All solvents used here were HPLC grade and were used without further purification. The solvent mixtures were prepared by mixing a known volume of each liquid. ET(33) was prepared and purified using a procedure given in the literature [25]. All spectroscopic measurements were made using a Varian DMS 200 spectrophotometer using a slit width of 0.2 nm, 20 nm/min scan rate, a smoothing constant of 5 s, and 1-cm pathlength quartz cells. The wavelength of the spectrophotometer was calibrated daily using a holmium oxide filter and the stability of the instrument throughout this experiment is indicated by no more than a 0.10 nm change in any of the six holmium oxide peaks monitored. All samples were thermostatted at 25 (± 0.2)°C for

15 min before scans were made and this included the holmium oxide filter. Each of the samples were gently rocked after sitting for 10 min in order to ensure temperature equilibrium throughout the sample. Peak maxima were determined using the "9/10" method in order to minimize the effect of changes in band shape with solvent [30]. Triplicate measurements of peak maxima agreed with one another within less than 0.5 nm. The indicator concentration was adjusted so as to give an absorbance in the range of 0.5 to 0.8 absorbance units. At this concentration it was confirmed that the peak maxima are independent on solute self-association.

3. Results and discussion

3.1. Solvatochromic comparison of $E_T(30)$ and $E_T(33)$

Although the absorption bands of ET(33) are at shorter wavelengths than those of ET(30), it exhibits almost the same shift with solvent in its electronic transition energy as does ET(30) [25]. Since the structure of ET(33) is very similar to ET(30) and thus will sense via its solvatochromic shift the same intermolecular interactions exerted by the solvent in a similar way to that of ET(30), we expected that the absorption energies of ET(33) would differ from those of ET(30) but that they would be *linearly* related as the volume fraction of organic modifier is varied. Plots of $E_T(33)$ vs. $E_T(30)$ for four different water–organic mixtures are shown in Fig. 1. The error bars indicate the random experimental error associated with determination of E_T. These plots are clearly not linear.

There are two potential simple explanations for the lack of linearity in such plots. First, as Kamlet et al. [31] have shown, $E_T(30)$ is actually a composite solvent characteristic. It actually responds to changes in both a solvent's dipolarity/polarizability, that is π^*, and a solvent's hydrogen bond donor strength, α.

$$E_T(30) = 31.00 + 13.43\pi^* + 15.06\alpha$$

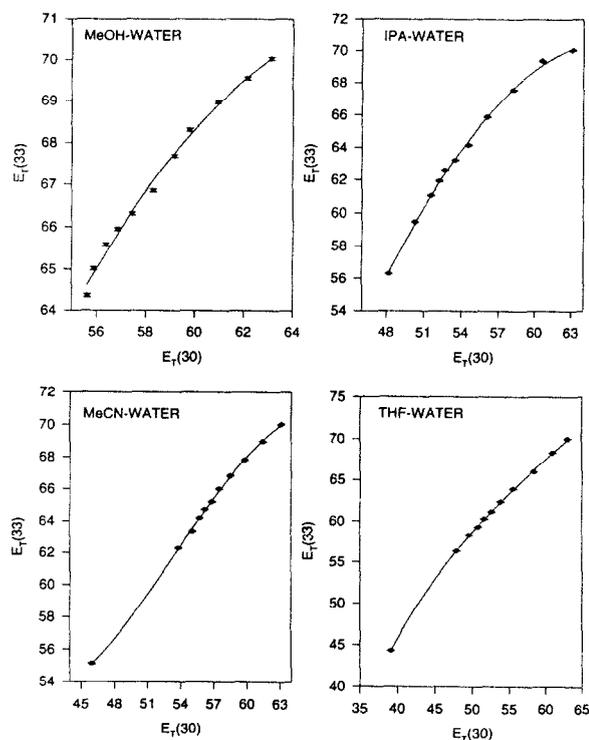$$N = 40, \text{ S.D.} = 1.65, r = 0.984$$

Fig. 1. Plots of $E_T(33)$ vs. $E_T(30)$ for aqueous mixtures of methanol (MeOH), acetonitrile (MeCN), isopropanol (IPA) and tetrahydrofuran (THF).

If ET(33) has a different blend of sensitivities to the solvent π^* and α then it would not respond linearly to plots of $E_T(30)$ vs. $E_T(33)$. In order to establish whether or not this is true we require a great deal of data on ET(33) in a series of pure solvents of known π^* and α. We will report on this elsewhere [32]. However, given the strong electron withdrawing effect of a chloro group it is quite possible that the sensitivities to π^* and α will be different for ET(30) and ET(33). Second, it is quite possible that the cybotactic region around the two dyes and especially at the O⁻ group could differ. It seems reasonable in view of the fact that a chloro group is a better electron acceptor than is a phenyl group that the relative amount of water in the solvent adjacent to the dye could differ for the two dyes. This results in a different effect on the solvatochromic shift of the two indicators.

In Fig. 2 *normalized* E_T values for ET(33),

$E_T^N(33)$, are plotted against corresponding $E_T^N(30)$ values for ET(30). The error bars indicate the size of the random experimental error. All the points in the plot lie below the 1:1 line. If solvation of the two dyes by the components in the aqueous mixture were to be the same all the points in the plot should fall on the 1:1 line. We believe that the deviations are probably due to preferential solvation, by which solvatochromic indicators are differentially solvated by one component of the hydro–organic mixtures. Preferential solvation has been widely reported [26,27,33–40]. A second possible explanation for the lack of agreement between the two indicators is microheterogeneity as discussed by Marcus and Migron [41–44]. Microheterogeneity refers to the state of incipient phase separation. That is the two components of the mixture on average prefer molecules of their own type. At this time we tentatively prefer to explain the systematic difference in behavior of the two indicators based on differential solvation. We do so because deviations from the 1:1 line (see Fig. 2) are least for the acetonitrile–water system which is the most non-ideal mixture and greatest for the two alcohol–water systems which are the more ideal mixtures. We will deal with the details of preferential solvation versus microheterogeneity elsewhere. As a consequence the polarity sensed by a single specific indicator in a water–organic mixture can not represent the average polarity which is sensed by various types of solutes.

The above data indicate that the theoretical interpretation of any single-parameter scale of solvent strength of hydro–organic mixtures is complex as is the interpretation of results based on such scales. Nonetheless single-parameter scales of solvent strength such as Snyder's S [48], the $E_T(30)$ scale or the $E_T(33)$ scale are undeniably very useful in practical chromatography.

3.2. Chromatographic comparison of $E_T(30)$ and $E_T(33)$

Table 1 lists the results of linear regressions for correlations between RPLC ln k' values and $E_T(30)$, $E_T(33)$ and volume fraction of organic
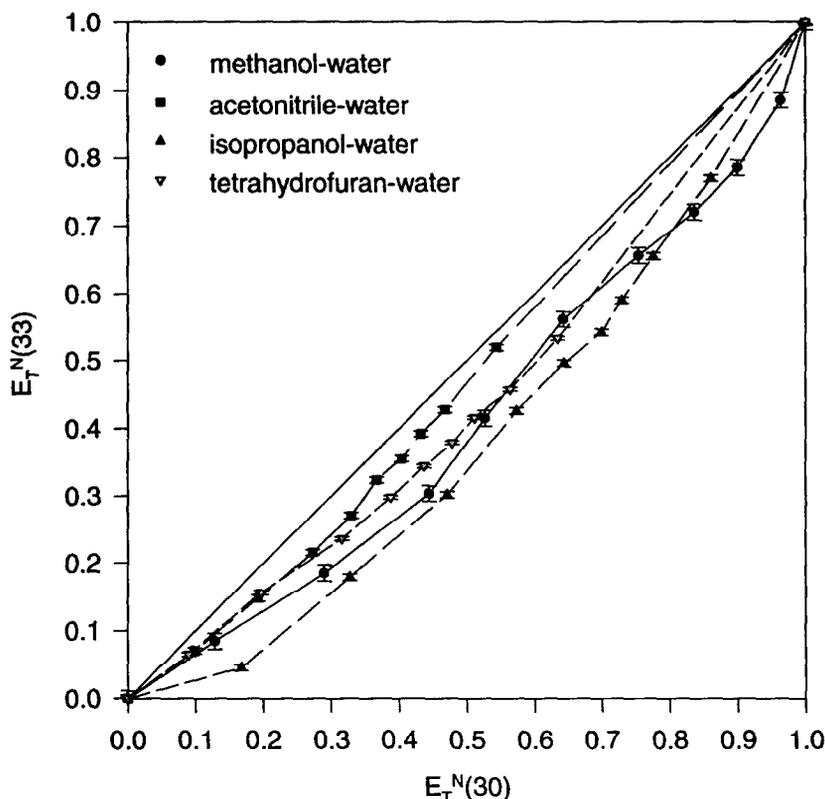
Fig. 2. Plot of $E_T^N(33)$ vs. $E_T^N(30)$ for aqueous mixtures of methanol, acetonitrile, isopropanol and tetrahydrofuran. E_T^N values are computed by the equation: $E_T^N = [E_T(\text{water}) - E_T(\phi_i)]/[E_T(\text{water}) - E_T(\text{pure organic})]$.

modifier (ϕ_0) for a number of solutes for an extended range of water–organic modifier compositions. In methanol–water mixtures correlations for non-polar solutes such as alkylbenzenes and naphthalene vs. $E_T(33)$ and ϕ_0 are better than those vs. $E_T(30)$. In contrast, for the polar solutes correlations with $E_T(30)$ are better than with $E_T(33)$ and ϕ_0. A similar trend is observed in acetonitrile–water mixtures. In isopropanol–water and tetrahydrofuran–water mixtures correlations with $E_T(30)$ are almost always better than with $E_T(33)$ and sometimes better than with ϕ_0. For the 332 ln k' data set Johnson et al. [14] reported an average r^2 of 0.9910 and average standard deviation of much less than 0.1 for plotting log k' vs. the mobile phases' $E_T(30)$ parameter, compared to an average r^2 of 0.9783 for plotting vs. volume percent organic modifier. However, their results were obtained with ln k'

data measured in mobile phases over a limited composition range. Only a few of the ranges were 70% and most were less than 50%. As can be seen in Table 1, r^2 values are much lower and standard deviations are much higher when the compositions of the mixtures are extended to the full range.

As expected from the non-linearity of plots of $E_T(33)$ vs. $E_T(30)$ (see Fig. 1) regression results with $E_T(33)$ are different from those with $E_T(30)$. Figs. 3 and 4 show plots of ln k' for a few selected solutes vs. $E_T(30)$ and $E_T(33)$, respectively. For a limited range in composition linearity is observed but curvature is evident if the entire range of the composition is examined. It can be argued that the curvature at low k' is an artifact due to an error in the void volume, but curvature is also observed in the range of high water content where retention is quite high.

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Table 1
Linear regression results for correlation between ln k' and either volume fraction, $E_T(30)$ or $E_T(33)$

Solute	Solvent/ % range	$E_T(30)$		$E_T(33)$		ϕ_0		n
		r^2	S.D.	r^2	S.D.	r^2	S.D.	
Benzene	MeOH/10–100	0.9737	0.292	0.9927	0.154	0.9998	0.024	10
Toluene		0.9918	0.231	0.9951	0.179	0.9921	0.227	10
Ethylbenzene		0.9847	0.344	0.9955	0.187	0.9970	0.151	10
Naphthalene		0.9649	0.708	0.9893	0.173	0.9998	0.048	10
Anisole		0.9954	0.208	0.9701	0.530	0.9488	0.694	10
Benzophenone		0.9986	0.132	0.9853	0.429	0.9712	0.600	10
Benzonitrile		0.9975	0.088	0.9906	0.171	0.9808	0.244	10
Phenol		0.9963	0.086	0.9925	0.122	0.9847	0.174	10
Benzene	MeCN/10–90	0.9827	0.218	0.9825	0.219	0.9836	0.212	9
Toluene		0.9827	0.257	0.9823	0.260	0.9832	0.253	9
Ethylbenzene		0.9820	0.278	0.9842	0.260	0.9877	0.229	9
Naphthalene		0.9778	0.269	0.9861	0.213	0.9953	0.123	9
Anisole		0.9768	0.263	0.9730	0.284	0.9719	0.289	9
Benzophenone		0.9825	0.298	0.9785	0.331	0.9756	0.352	9
Benzonitrile		0.9822	0.203	0.9773	0.229	0.9735	0.247	9
Phenol		0.9720	0.221	0.9560	0.277	0.9415	0.320	9
Benzene	THF/10–90	0.9860	0.238	0.9857	0.240	0.9728	0.332	9
Toluene		0.9861	0.272	0.9849	0.284	0.9704	0.399	9
Ethylbenzene		0.9855	0.289	0.9870	0.274	0.9778	0.358	9
Naphthalene		0.9855	0.322	0.9814	0.365	0.9609	0.529	9
Anisole		0.9861	0.238	0.9836	0.258	0.9663	0.370	9
Benzophenone		0.9852	0.302	0.9805	0.347	0.9587	0.505	9
Benzonitrile		0.9861	0.190	0.9853	0.195	0.9716	0.272	9
Phenol		0.9861	0.192	0.9850	0.199	0.9704	0.280	9
Benzene	THF/30–90	0.9841	0.076	0.9766	0.093	0.9908	0.058	7
Toluene		0.9835	0.091	0.9755	0.110	0.9872	0.079	7
Ethylbenzene		0.9721	0.131	0.9617	0.153	0.9766	0.120	7
Propylbenzene		0.9692	0.154	0.9587	0.179	0.9720	0.147	7
Butylbenzene	THF/40–90	0.9496	0.169	0.9392	0.185	0.9819	0.101	6
Benzene	IPA/30–100	0.9139	0.171	0.8464	0.229	0.9665	0.107	8
Toluene		0.9216	0.190	0.8550	0.259	0.9657	0.126	8
Ethylbenzene		0.9225	0.214	0.8559	0.292	0.9617	0.150	8
Propylbenzene		0.9213	0.244	0.8537	0.333	0.9568	0.181	8
Butylbenzene		0.9207	0.272	0.8526	0.371	0.9528	0.210	8

Capacity factor data are from refs. [45–47].

It is also observed that the amount of curvature in the correlations varies systematically with the test solutes. Systematic failure for such non-polar and non-hydrogen bonding solutes as alkylben- zenes and naphthalene is a strong indication that any single-parameter solvent scale should not be used for correlation of RPLC retention data for the full range of composition and subsequent

MeOH-Water

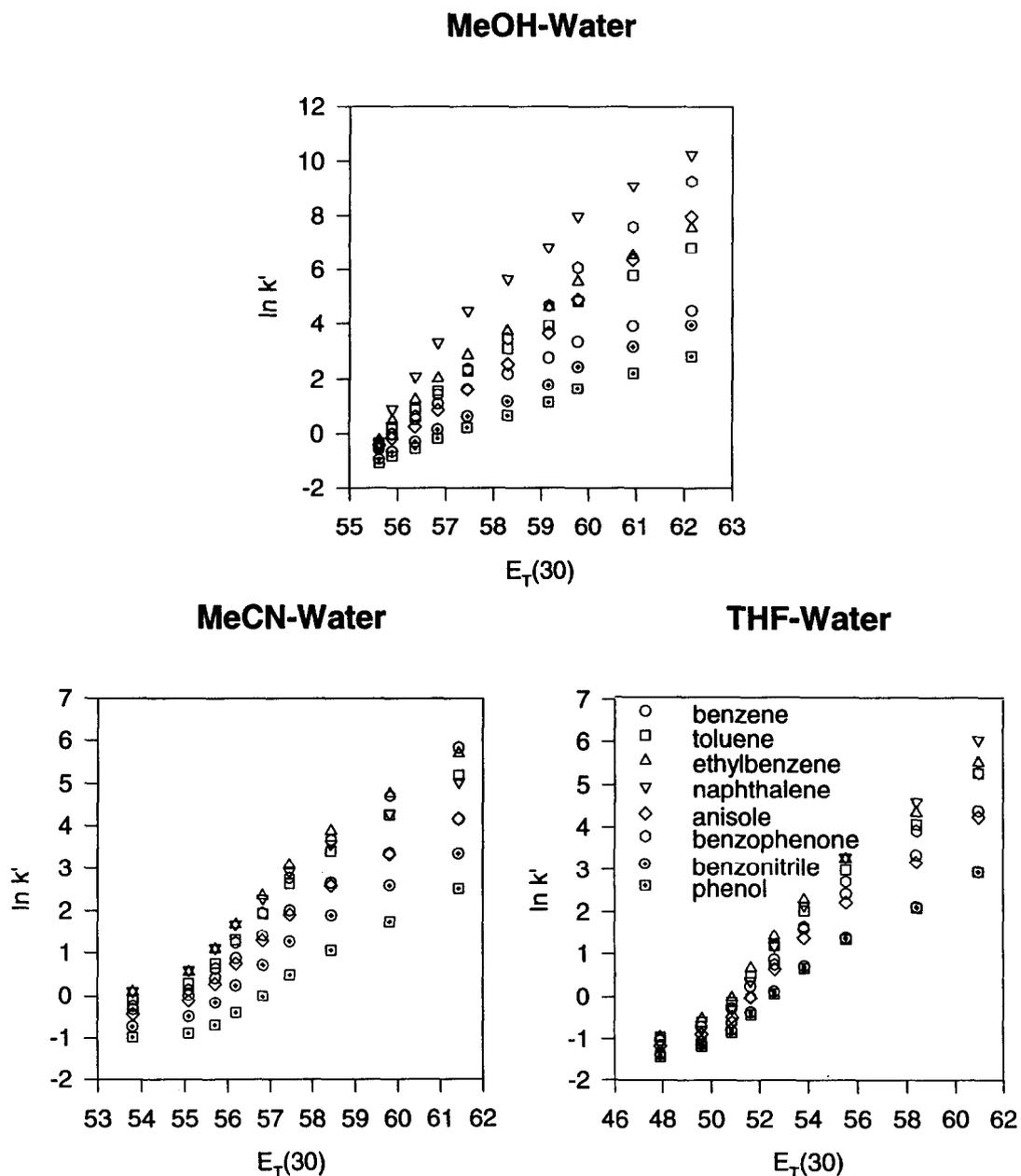## MeCN-Water   THF-Water

Fig. 3. Plots of logarithmic capacity factor vs. $E_T(30)$ for aqueous mixtures of methanol, acetonitrile and tetrahydrofuran. Symbols are shown in the THF–water plot.

theoretical interpretation of the meaning of the regression coefficients based on those regressions.

Although no specific results are given here we examined the effect of using the $E_T(33)$ scale as a basis for extrapolation to pure water eluent to
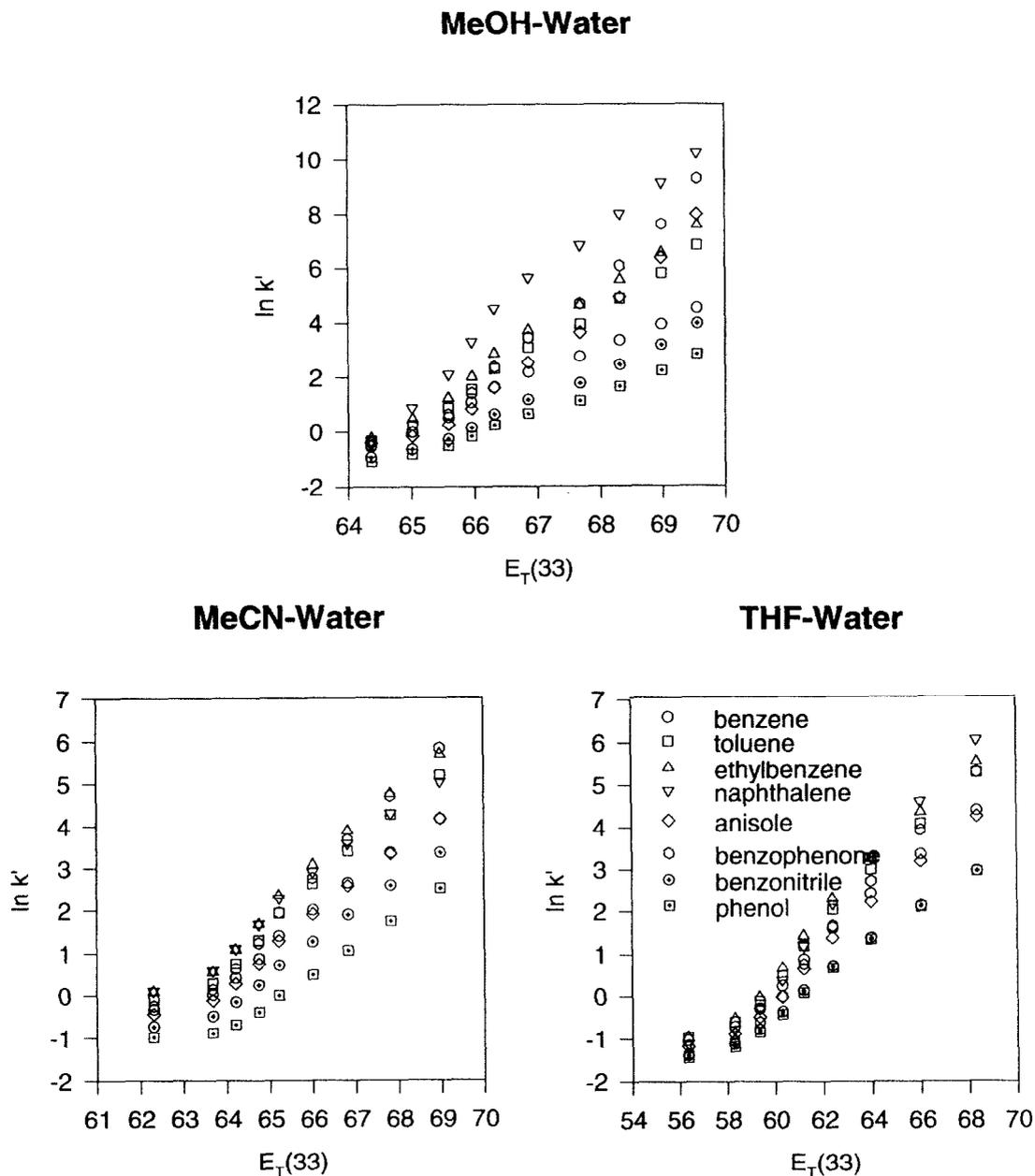
MeOH-Water

MeCN-Water

THF-Water

Fig. 4. Plots of logarithmic capacity factor vs. $E_T(33)$ for aqueous mixtures of methanol, acetonitrile and tetrahydrofuran. Symbols are shown in the THF–water plot.

obtain log k_w' values. As expected in many cases we observed that statistically different log k_w' values are obtained depending on whether the ET(30) or ET(33) scales are used. Thus we again caution against the use of any single-parameter scale for the elucidation of either thermodynamic or kinetic studies [23,24] in mixed aqueous organic media.

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