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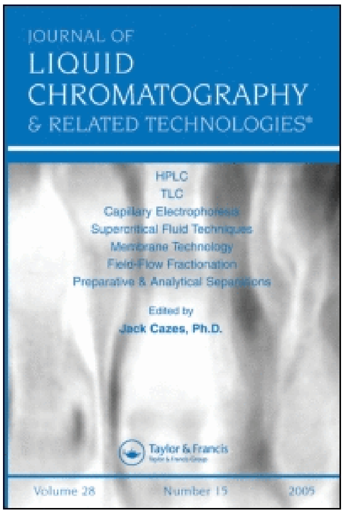

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The Surface Tension of Mixtures of Methanol, Acetonitrile, Tetrahydrofuran, Isopropanol, Tertiary Butanol and Dimethyl-Sulfoxide with Water at 25°C

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THE SURFACE TENSION OF MIXTURES OF METHANOL, ACETONITRILE, TETRAHYDROFURAN, ISOPROPANOL, TERTIARY BUTANOL AND DIMETHYLSULFOXIDE WITH WATER AT 25°C

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ABSTRACT

Surface tension data of binary mixtures of methanol ,acetonitrile, tetrahydrofuran, isopropanol, tertiary butanol and dimethylsulfoxide with water have been measured. Best fit polynomal functions are reported for ln σ vs. volume fraction of an organic modifier. The reported data is precise and accurate to about 2 % and is consistent with the available literature data. The sequence of eluotropic strength based on the solvophobic theory in RP-HPLC should be dimethylsulfoxide < methanol < acetonitrile <THF (tetrahydrofuran) <IPA (isopropanol) < tertiary butanol based on the results of this study.

INTRODUCTION

Surface tension has been employed as a key parameter in several of the major approaches to the theory of retention in reversed phase liquid chromatography.(1-6) Despite this considerable level of theoretical interest, there is only a rela-

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tively small body of data available on the surface tension of aqueous mixtures with the organic modifiers which are commonly employed in reversed phase liquid chromatography. Even if these theories are approximate surface tension data should serve as a qualitative guide to estimating relative eluotropic strength. In view of the importance of reliable self-consistent data for the surface tension of common RP-HPLC eluents , we measured the values at 25°C over a wide range in compositions. The ring tensiometric method was used in this study. This approach has been widely used for measurements of liquids(7)since Harkins and Jordan (8) improved the accuracy and established the necessary correction factor tables based on the theoretical work of Freud and Freud(9).

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MATERIALS

All the solvents used in this study were HPLC grade (Aldrich Chem Co.); except for tertiary butanol and DMSO the purities exceeded 99.9%. , the major impurity being water. The DMSO and butanol were 99.8 and 99.5% pure respectively. Laboratory deionized water was further purified by use of a NANOpure II water purification system (Sybron/Barnsted Co.) which includes a carbon filter as the last stage to remove nonpolar organics. In all cases the water employed had a resistivity greater than 16.7 mega ohms. Because traces of surface active agents can greatly influence the surface tension extreme care was taken in cleaning the glassware. A commercial cleaning powder , NoChrom (Godax Lab.

Inc.), dissolved in concentrated sulfuric acid was used. Glassware was cleaned with this solution and thoroughly rinsed with ultrapure water and with HPLC grade methanol and finally dried overnight. In general we found excellent agreement with the literature value of the surface tension of water ,which is known to be very sensitive to traces of organic materials, thereby indicating that the procedure used to clean the glassware was adequate.

METHODS

Details of the experimental methods can be found elsewhere (8). The original design of the apparatus , however, was modified as per the following description. The surface tension which generates a downward force on the ring and therefore on the balance is directly converted to an electronic signal via a Cahn Electrobalance. The signal is observed on a Gould recorder (Model 15-4228-10). Instead of a sample flask , a disk type sample vessel was used. The vessel is placed on top of an elevator located in a cabinet below the balance. The elevator is actuated by a manual air pump. The whole unit (the balance, the cabinet, the air pump element and the frame) is placed in a large air bath. Temperature control elements are installed in the upper portion of the air bath. The air box is comprised of a set of transparent and styrofoam panels. The transparent front has two holes to allow for sample insertion and air pump handling. The cooling coil is connected to a thermostated water bath (Forma scientific, Model

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2095). Temperature is monitored by a digital thermometer (Instrulab, Model 4606-30-03). The air box temperature is maintained at 25±0.05° by a temperature controller (Yellow Springs Instrument Co., Model 72). The circumference of the ring (Central Scientific Co., No. 70532) used in this work is 5.992 cm and the ratio of radius to thickness is 53.6.

The measurement procedure is as follows : 1) Samples to be measured are placed in the air box. 2) After thermal equilibrium is achieved, a sample is poured in the disk-type sample vessel. The door of the cabinet is opened and the beaker is placed on top of the elevator. The ring is flame-dried and installed. 3) The door is closed. The sample is left for 10-15 minutes to allow liquid-vapor equilibrium to be achieved. 4) The elevator is raised until the ring is immersed. It is then released slowly. The force acting on the balance is recorded with respect to time. The maximum value of the downward force is used to calculate the surface tension. All measurements were repeated 3-5 times. The reproducibility of replicate measurements on the same sample is excellent (±0.1 %).

Samples were prepared, using carefully cleaned volumetric pipets, in glass stoppered 100 ml volumetric flasks and then wrapped with parafilm. Two to four replicate batches of each sample were prepared. The average of the replictes and the standard deviations of the measurements on separately prepared samples are reported in Table 1. In order to make the results most directly meaningful for liquid chromatography the mixture composition is reported as the volume fraction defined below:

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$$\text{volume \%} = 100 \; V_o \; / \; (V_o + V_w) \qquad (1)$$

where V_o is the volume of the relevant organic solvent and V_w is the volume of water before mixing at 25°C.

RESULTS

The results of the measurements are summarized in Table 1. In order to allow for easy comparison of qualitative differences in the mixtures a reduced surface tension was computed as defined below:

$$\bar{\sigma} = (\sigma - \sigma_o) \; / \; (\sigma_w - \sigma_o) \qquad (2)$$

where σ is surface tension of mixture , σ_w , that of water and σ_o , that of the pure organic co-solvent .

Relative standard deviations for samples prepared and measured on different days is always less than 2 % (generally less than 1%) for all measurements. Also included are the density data of the same solvent mixtures at 25°C. Density data for the MeOH /water, MeCN/water , t-BuOH/water , and DMSO/water systems were obtained from reference (10), for IPA/H_2O , from reference (11), and for THF/H_2O , from reference (12). The raw data were processed so that appropriately fitted polynomial functions were derived and used to calculate the density values for various mixture compositions in Table 1. Surface tension data for pure solvents are separately shown in Table 2 along with the available literature data.

Plots of the reduced surface tension vs. volume fraction organic are shown in Figure 1.

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TABLE 1
Surface Tension Data of Common Binary RP-HPLC Solvents at 25 °C(σ ; dyne/cm)

vol. % of the org. component	property[a]	system					
		MeOH	MeCN	IPA	THF	t-BuOH	DMSO
5	σ	62.8	60.6	49.5	53.2	42.8	68.2
	s.d. of σ	0.09	0.28	0.65	0.04	0.15	0.05
	$\bar{\sigma}$	0.821	0.743	0.565	0.587	0.442	0.881
	d	0.990	0.991	0.992	0.996	0.991	1.004
10	σ	57.3	52.8	41.2	46.1	35.0	66.6
	s.d. of σ	0.12	0.25	0.48	0.50	0.10	0.12
	$\bar{\sigma}$	0.709	0.562	0.400	0.430	0.292	0.826
	d	0.984	0.985	0.987	0.994	0.986	1.011
15	σ	53.0	46.7	35.8	41.3	29.9	65.3
	s.d. of σ	0.41	0.20	0.04	0.32	0.09	0.10
	$\bar{\sigma}$	0.621	0.422	0.294	0.323	0.192	0.779
	d	0.977	0.977	0.980	0.992	0.980	1.018
20	σ	49.1	42.5	32.0	38.1	26.5	64.2
	s.d. of σ	0.33	0.26	0.11	0.06	0.04	0.08
	$\bar{\sigma}$	0.543	0.324	0.220	0.251	0.127	0.743
	d	0.971	0.969	0.973	0.989	0.972	1.026
30	σ	43.3	37.1	27.3	33.7	23.8	62.0
	s.d. of σ	0.11	0.23	0.03	0.11	0.06	0.04
	$\bar{\sigma}$	0.424	0.200	0.127	0.152	0.074	0.667
	d	0.957	0.950	0.957	0.982	0.956	1.042
40	σ	38.7	34.2	25.4	31.7	22.9	60.0
	s.d. of σ	0.23	0.15	0.16	0.20	0.04	0.05
	$\bar{\sigma}$	0.332	0.133	0.091	0.107	0.058	0.598
	d	0.941	0.929	0.938	0.974	0.936	1.058
50	σ	35.4	33.1	24.5	30.4	22.7	57.4
	s.d. of σ	0.46	0.04	0.03	0.08	0.02	0.03
	$\bar{\sigma}$	0.266	0.107	0.073	0.079	0.053	0.509
	d	0.923	0.906	0.917	0.963	0.914	1.072
60	σ	32.6	32.4	24.0	29.7	22.3	55.1
	s.d. of σ	0.43	0.07	0.03	0.12	0.05	0.06
	$\bar{\sigma}$	0.207	0.090	0.062	0.063	0.045	0.428
	d	0.903	0.882	0.894	0.951	0.891	1.085
70	σ	30.0	31.9	23.4	29.2	22.1	52.0
	s.d. of σ	0.25	0.08	0.02	0.14	0.04	0.05
	$\bar{\sigma}$	0.155	0.079	0.050	0.053	0.042	0.323
	d	0.880	0.857	0.868	0.936	0.865	1.094
80	σ	27.4	31.3	22.7	28.8	21.5	48.5
	s.d. of σ	0.10	0.17	0.07	0.06	0.02	0.13
	$\bar{\sigma}$	0.103	0.065	0.038	0.043	0.031	0.200
	d	0.853	0.830	0.841	0.920	0.838	1.099
90	σ	25.0	30.4	21.9	28.3	20.9	45.7
	s.d. of σ	0.06	0.18	0.15	0.07	0.04	0.04
	$\bar{\sigma}$	0.055	0.043	0.021	0.032	0.018	0.104
	d	0.822	0.804	0.812	0.902	0.811	1.100

a. Surface tension(dyne/cm), its standard deviation, the reduced surface tension (see Eqn. 2), and the density(gm/cc) at 25°C

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TABLE 2
Surface Tension and Density Data for Pure Solvents(σ ;dyne/cm)

solvent	surface tension^{a,b}	density	source
water	71.66±0.27		this study
	71.81	0.99705	(13)
	71.97±0.05		(14)
MeOH	22.35		this study
	22.30(20), 22.09*^{c}, 21.69(30)	0.78664	(13)
	22.61±0.1(20)		(14)
	22.09-22.2		(11)
MeCN	28.49		this study
	29.10(20), 28.5*, 27.80(30)	0.7766	(13)
	29.30(20)		(14)
	28.37(20)		(11)
IPA	20.82		this study
	21.79(15), 21.2*, 27.80(30)	0.78126	(13)
	21.7±0.3(20)		(14)
THF	26.88		this study
	26.4	0.8892(20)	(13)
	27.64(20)		(14)
		0.8811	(12)
t-BuOH	19.93		this study
	20.02(26)	0.7812	(13)
	20.7±0.5(20)		(14)
DMSO	42.70		this study
	42.86	1.0958	(13)

a. All measurements from our work are at 25°C.

b. For the data not at 25°C the temperature is given in parentheses.

c. An asterik indicates that the datum was obtained by interpolation from literature data.

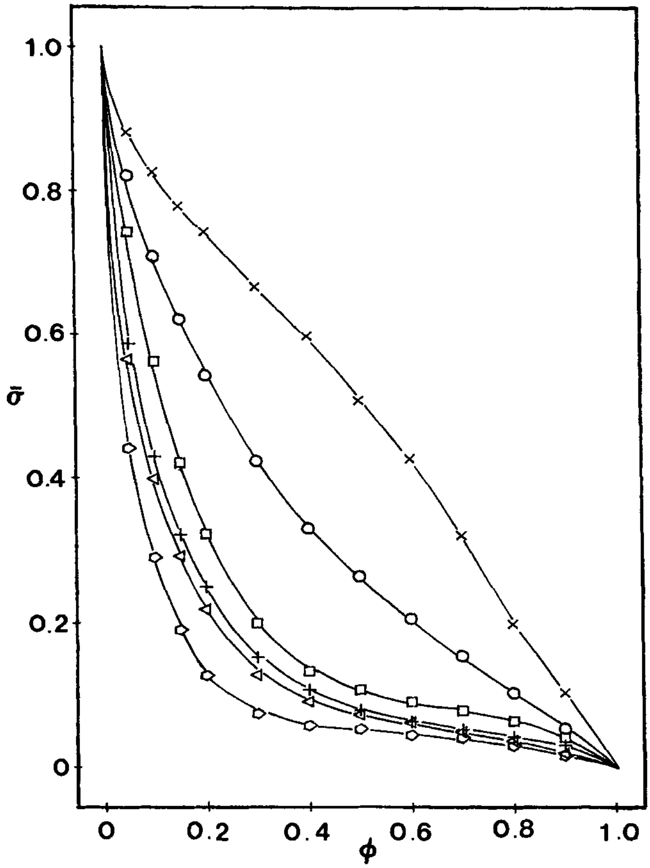

FIGURE 1. The Plots of the Reduced Surface Tension vs. the Volume Fraction of the Organic Component at 25°C (X ;DMSO/water, ○ ; MeOH/water, □ ;MeCN/water, +; THF/water, ◁ ; IPA/water, ⬡ ;t-BuOH/water) .

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DISCUSSION

Comparison of the measured data (25 °C) with literature results leads to some disagreements. Literature data on the surface tension of mixtures of organic solvents with water are scarce except for $MeOH/H_2O$ mixtures (11).

For the $MeOH/H_2O$ system, we observed good agreement between the measured and literature data. For $MeCN/H_2O$ and IPA/H_2O systems, rather large discrepancies were observed. Only one data set has been reported at 20°C for each system(11). It should be noted that these data sets are questionable. In Table 2, the measured and literature data on the surface tension of the pure solvents are listed. Asterisks indicate that the data were obtained by interpolation from literature data. The temperature is 25°C unless denoted by a value in parentheses. As is seen in Table 2 , the surface tension data of pure acetonitrile at 20°C from reference (11) is not in agreement with those from references (13) and (14). It is possible that the purity of the acetonitrile used in reference (11) was not equivalent to that used herein. For the THF/H_2O system , we found that the significant discrepancy in the pattern of the dependence of surface tension with respect to volume percent between our measurements and literature data (11) disappeared when a possible misprint (weight % for mole %) in the literature data set was corrected.

Examination of Table 2 leads to the conclusion that the differences between our results and those of reference (13) for pure solvents at 25°C are less than 2% .

An unique observation is that surface tension first decreases quite abruptly as the volume percent of the organic solvent increases and subsequently the rate of change decreases and again becomes rather steep in the region of greater than 90% organic solvent. This phenomenon is quite clear for the mixtures containing acetonitrile, IPA, t-butanol and THF (Figure 1). This pattern is also observed for the ethanol-water system from several sources [(11)]. It is also very interesting to note that in terms of the reduced surface tension (see Figure 1) there are no "cross overs" in the variation with the volume fraction of the organic solvent. In contrast several changes in the order of solvents are observed in the surface tension per se in the region above 70% organic solvent.

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Based on the ability of the organic modifier to decrease the surface tension of water upon addition of a small amount (10% by volume), the sequence of eluotropic strengths in reversed phase liquid chromatography should be DMSO < MeOH < MeCN < THF < IPA < t-butanol. This is in distinct contrast to the order of surface tensions of the pure organic solvents--DMSO > MeCN > THF > MeOH > IPA > t-butanol. Based on our data there is evidently only a rough correlation between the surface tension of the pure solvent and its ability to decrease either the surface tension or the reduced surface tension of pure water.

Clearly the chemical effect of adding the solvent is not merely dilution of the higher surface tension liquid, i.e. water, with a lower surface tension material. The distinct nonlinearity and lack of overlap in the plots of the reduced surface tension support this view (see Figure 1). If the solvents acted simply as diluents all of the reduced surface tension curves would overlap. In contrast we see a complex pattern. In most cases the curves are quite concave. DMSO behaves quite differently from the other organic liquids.

In order to facilitate interpolation of this data to compositions for which measuremnets were not made the data were fitted to polynomial functions. We found that considerably fewer terms were needed to fit the logarithm of the surafce tension than were needed for the surface tension per se with the same accuracy. The order of the polynomial was established by increasing the number of terms until no improvement was obtained in the sum of residuals as shown by an F-ratio test(See Table 3c). The best fit polynomial functions are reported in Table 3a and 3b. The polynomial functions are defined as follows:

$$\ln(\sigma) = A + \sum_{i=1}^{m} B_i x^i \qquad (3)$$

Even the logarithm of the surface tension is a distinctly nonlinear function of the volume fraction and quite a few terms are needed for accurate interpolation. Two different curve sets of coefficients are given in Table 3a and 3b. The first set of coefficients is based on the entire range (volume fraction 0 to 1.0). The other covers data points in the range from 0.2 to 0.8 volume fraction, which is the range of practical importance in RP-HPLC. We advise that the second set be employed in this range of compositions.

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TABLE 3a
Best Fit Polynomial Functions for ln σ vs Volume Fration(x:0-1.0)

system	MeOH / water	MeCN / water	IPA / water	THF / water	t-BuOH / water	DMSO / water
A	4.258	4.273	4.237	4.254	4.239	4.266
s.d.	0.006	0.002	0.023	0.016	0.030	0.004
B1	-2.226	-3.683	-6.363	-5.796	-9.943	-0.812
s.d.	0.057	0.036	0.356	0.378	0.709	0.064
B2	2.277	6.140	14.85	18.82	36.12	1.870
s.d.	0.139	0.158	1.556	2.651	4.972	0.280
B3	-1.204	-4.164	-15.31	-33.50	-64.39	-2.793
s.d.	0.092	0.245	2.415	7.174	13.46	0.434
B4	_	0.784	5.630	30.01	55.19	1.224
s.d.		0.122	1.208	8.156	15.30	0.217
B5	_	_	_	-10.50	-18.23	_
s.d.				3.280	6.152	
r	0.99985	0.99997	0.99834	0.99896	0.99764	0.99972
s	0.0075	0.0026	0.0261	0.0175	0.0328	0.0047

r ; correlation coefficient
s ; root mean square residual in ln σ

We are not aware of any theoretical model which can accurately relate the variation in surface tension of mixtures of water with less polar solvents to the composition of the mixture. The above polynomial fits are provided only for the purpose of interpolation and are not based on any principle. In contrast several groups have attempted to relate the solubility parameter of a mixture to that of the pure component liquids (15,16). Because surface tension and solubility parameter are, as demonstrated by Beerbower, closely correlated, at least for simple liquids (17,18)

TABLE 3b

Best Fit Polynomial Functions for ln σ vs Volume Fraction(x:0.2-0.8)

system	MeOH / water	MeCN / water	IPA / water	THF / water	t-BuOH / water	DMSO / water
A	4.252	4.247	4.311	4.052	3.676	4.245
s.d.	0.013	0.021	0.042	0.031	0.059	0.015
B1	-2.181	-3.420	-6.843	-2.801	-2.901	-0.486
s.d.	0.092	0.153	0.416	0.225	0.421	0.106
B2	2.226	5.194	16.30	4.090	5.005	0.488
s.d.	0.199	0.329	1.418	0.486	0.909	0.228
B3	-1.212	-2.720	-17.64	-2.088	-2.913	-0.561
s.d.	0.132	0.218	2.001	0.322	0.602	0.151
B4	–	–	7.046	–	–	–
s.d.			0.998			
r	0.99998	0.99978	0.99995	0.99943	0.99583	0.99988
s	0.0019	0.0032	0.0021	0.0047	0.0088	0.0022

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there might be some possiblities along the direction of this analogy for mixtures of nonpolar liquids. However the systems employed here are likely too complex to be described by any simple theory. It is very likely that the polar functional groups of water, and the alcohols will self-associate in the surface region and orient themselves towards the bulk liquid. Similarly it is likely that the less polar groups would be forced to orient themselves towards the air side of the interface. For exactly the above reasons it is likely that the surface tension rather than a bulk property may be a more useful predictor of solvent strength in reversed phase chromatography at least for nonpolar solutes.

TABLE 3c

The F Values Calculated for the Estimation of the Best Fit Polynomial Functions.

		$<F_{calc}>$[a]						$<F_{1,n-k,0.05}>$[b]
	k[c]	MeOH / water	MeCN / water	IPA / water	THF / water	t-BuOH / water	DMSO / water	
n=13[d]	4	170	1189	51.0	45.6	28.7	9.25	5.12
	5	4.83	41.1	21.7	11.5	22.4	31.7	5.32
	6	3.91	0.127	4.93	10.2	8.78	2.18	5.59
	7	1.29	3.058	3.49	4.16	3.66	-	5.99
	8	-	-	-	-	2.49	-	6.61
n=7[e]	3	17.0	25.6	13.4	30.5	6.53	54.2	7.71
	4	84.3	155	34.8	42.0	23.4	13.8	10.13
	5	-	1.81	50.0	10.8	4.98	0.22	18.51
	6	-[f]	-	-	-	-	-	-

a. $(S_{k-1}-S_k)(n-k)/S_k$. S_k; the sum of squared residuals for the polynomial function composed of k terms.
b. F values from reference (22).
c. number of terms of the polynomial functions.
d. volume fraction; 0-1.0 , n; number of data points.
e. volume fraction; 0.2-0.8.
f. no entry when $S_k>S_{k-1}$.

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That is the orientation of the component functional groups of a solvent molecules about a solute may more closely resemble their orientation at an interface than in the bulk fluid.

The Gibbs isotherm relationship can be used to examine the data in somewhat greater detail (19,20). It can be shown with thermodynamic rigor that the surface excess of a species in a mixture, denoted Γ , is related to the change in surface tension by the following equation:

$$\Gamma = \frac{-\, d\sigma}{RT\, d\ln(a)} \qquad (4)$$

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where a represent the activity of the species of interest in the bulk phase, R is the gas constant and T is the temperature. Based on the assumption that at low concentration Henry's law applies to the organic co-solvent it follows, using the pure substance standard state, that:

$$a = K_H X \qquad (5)$$

At very low concentration of organic solvent the activity coefficient of the organic material will be independent of concentration and thus a plot of surface tension versus the logarithm of the mole fraction will be a straight line if the surface excess is constant. Such plots are given in Figure 2. It is evident that they are far from linear. We extended the range of data for t-butanol by measuring values at volume fractions of 0.00514, 0.0108, 0.0201, 0.0299, 0.0314, and 0.0697. Even these curves are quite nonlinear at low concentration. It is evident that the surface phenomena involved are very complicated. It is likely that adsorption of the organic modifier into nonpolar bonded phases will also be complex.

In the absence of a detailed theoretical model it is often useful to examine thermodynamic data in terms of excess quantities. In general an excess property is defined as the difference between that of the mixture and that expected on the basis of ideal (random) mixing. By analogy we define the excess surface tension as follows:

$$\sigma^E = \sigma - (\sigma_o \phi_o + \sigma_w \phi_w) \qquad (6)$$

In equation (6), E denotes the excess property, o, the organic solvent, and w, water. Note that we decided to present the excess

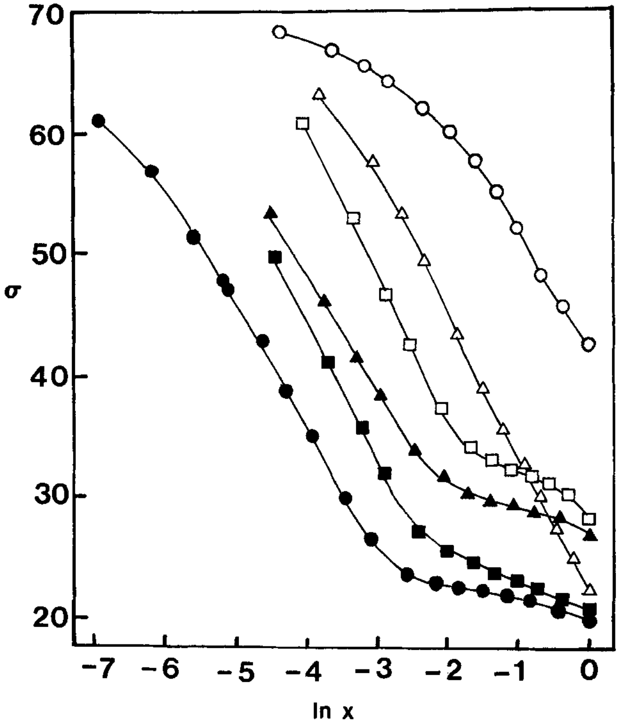

FIGURE 2. The Plots of the Surface Tension vs. the Logarithm of the Mole Fraction of the Organic Component at 25°C (○;DMSO/water, △ ;MeOH/water, □ ;MeCN/water, ▲ ;THF/water, ■ ;IPA/water, ● ;t-BuOH/water) . ;[dyne/cm]

surface tension as based on the volume fraction. Generally excess properties (G^E, H^E, S^E etc.) are based on mole fraction. The calculated volume-fraction-based excess surface tensions are listed in Table 4. We opted for the above definition because the data were collected as a function of volume fraction.

The excess surface tensions are plotted with respect to volume fraction in Figure 3. The plot shows that the order of

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TABLE 4
Volume-Fraction-Based Excess Surface Tensions(dyne/cm)

volume fraction	MeOH / water	MeCN / water	IPA / water	THF / water	t-BuOH / water	DMSO / water
0	0	0	0	0	0	0
0.05	-6.38	-8.94	-19.59	-16.27	-26.30	-2.00
0.1	-9.43	-14.58	-25.43	-21.04	-31.47	-2.13
0.15	-11.27	-18.48	-28.26	-23.60	-34.03	-2.06
0.2	-12.66	-20.54	-29.50	-24.59	-34.83	-1.65
0.3	-13.61	-21.59	-29.16	-24.54	-32.39	-0.94
0.4	-13.24	-20.16	-25.89	-22.10	-28.03	-0.07
0.5	-11.57	-16.99	-21.71	-18.84	-23.13	0.26
0.6	-9.52	-13.40	-17.21	-15.07	-18.36	0.82
0.7	-7.16	-9.55	-12.71	-11.07	-13.37	0.65
0.8	-4.79	-5.83	-8.26	-7.03	-8.77	-0.01
0.9	-2.24	-2.45	-4.01	-3.05	-4.23	0.10
1	0	0	0	0	0	0

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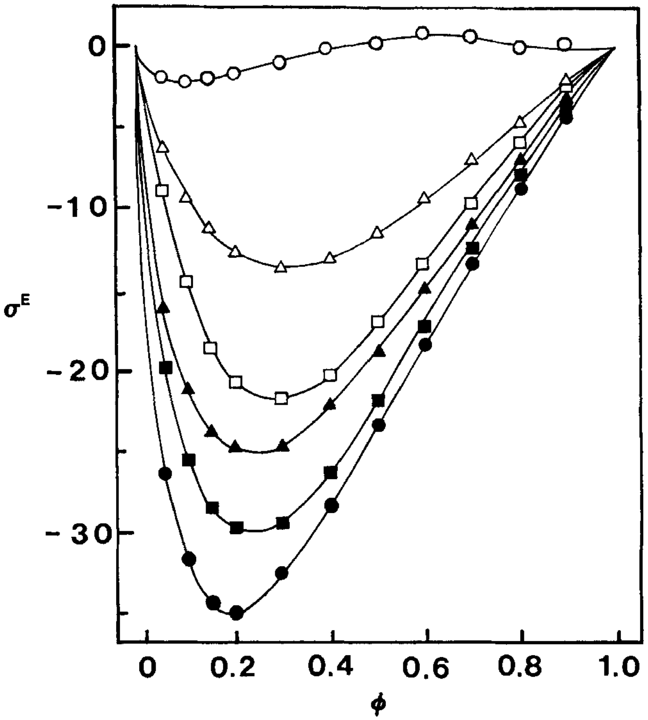

FIGURE 3. The Plots of the Excess Surface Tension vs. the Volume Fraction of the Organic Component at 25°C (○ ;DMSO/water, △ ;MeOH/water, □ ;MeCN/water, ▲ ;THF/water, ■ ;IPA/water, ● ;t-BuOH/water)

magnitude of deviation from additivity is t-butanol> IPA> THF> MeCN> MeOH> DMSO, which is in agreement with the order of eluotropic strength previously discussed. With the exception of DMSO all five plots are similar in that negative excess mixing is observed and a maximum occurs well before 50% volume. This clearly indicates that the organic modifier is being concentrated into the solution/air interface in preference to water. According to regular solution theory, which applies to mixtures having no excess volume and entropy of mixing, the maximum in this plot would occur at 50% volume. The above result i.e. a maximum at low fraction organic modifier also occurs if the data are presented in terms of the mole fraction.

The excess surface tensions were fitted by least squares polynomial regression to Margules type expressions (21) . We

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TABLE 5
Regression Results of the Correlation by Eqn.(7)

coefficients	MeOH / water	MeCN / water	IPA / water	THF / water	t-BuOH / water	DMSO / water
A	-42.9	-66.4	-70.2	-61.4	66.6	3.85
s.d.	3.6	2.3	17.0	14.5	26.8	2.34
B	-48.3	-82.1	-143.5	-120.2	-184.6	-14.6
s.d.	4.3	2.7	19.8	16.8	31.3	2.7
C	-41.2	-49.1	-178.5	-141.9	-261.1	-29.0
s.d.	9.0	5.7	41.6	35.4	65.8	5.7
r	0.981	0.997	0.963	0.960	0.950	0.954
s	7.55	4.78	34.85	29.7	55.10	4.80

r; correlation coefficient
s; root mean square residual in $\sigma^E/\phi\,(1-\phi)$

found that the curves are quite complex and in general a high order polynomial is required to fit the data.

$$\sigma^E = (1-\phi)(\phi)\ [\ A + B\ (1-2\phi) + C\ (1-2\phi)^2\ ] \qquad (7)$$

The regression results are summarized in Table 5.

In the future we will assess the applicability of the above data to the correlation of capacity factors in reversed phase liquid chromatography and the activity coefficients of nonpolar solutes in the mobile phase.

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