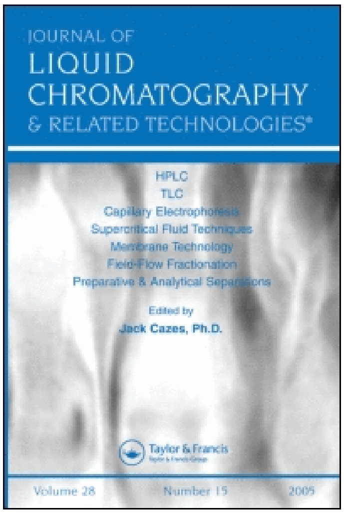

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Determination of Solvent Basicity Scale, β, of Mixed Solvents for Three Chromatographic Solvent Systems: 2-Propanol/Hexane, Ethyl Acetate/Hexane, and Methanol/Water

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DETERMINATION OF SOLVENT BASICITY SCALE, β, OF MIXED SOLVENTS FOR THREE CHROMATOGRAPHIC SOLVENT SYSTEMS: 2-PROPANOL/HEXANE, ETHYL ACETATE/HEXANE, AND METHANOL/WATER

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ABSTRACT

We have determined β values of mixed solvents for the 2-propanol/hexane, ethyl acetate/hexane, and methanol/water systems using totally 5 indicator pairs (10 dyes) three of which were synthesized in this study. The variations of β vs. solvent composition for the RPLC solvent system are in a striking constrast with those for the NPLC systems. While a definite maximum was recognized in the plots of β vs. ϕ for the NPLC systems, a linear correlation of β with ϕ was observed for the RPLC solvent system. The appearance of maximum is probably due to formation of aggregates of the more polar solvent when its composition gets higher.

INTRODUCTION

Linear solvation energy comparison methods based on Kamlet/Taft polarity scales[1-5] have been known to be very useful in exploring linear solvation energy relationships (LSER) in reverse phase liquid chromatography (RPLC)[6-12]. Application of LSER to normal phase liquid chromatography (NPLC)[13] has been recently reported, too. The basic idea of such approaches is that a distribution of a solute between two immisicible phases is governed by the cavity formation energy of the solute and by the solute-solvent interaction energies in each phase and that the solute-solvent interaction energies are the linear sum of several independent terms each of which corresponds to a characteristic solute-solvent interaction. Each interaction energy is proportional to the cross product of the semiempirical polarities of the solute and the solvent.

In LSER studies of chromatography, one needs polarity data of mixed solvents. Some research groups have reported polarity scales of mixed solvents for RPLC[14-16] and NPLC[17-18].

In this study, hydrogen bond accepting basicity (β) values of binary solvents have been determined for a typical RPLC solvent system (methanol/water) and two NPLC solvent systems (2-propanol/ hexane and ethyl acetate/hexane) using five pairs of indicator dyes three of which were directly synthesized in this study. Determination of β is based on the assumption that β is linearly correlated with the difference between absorption frequencies of a pair of indicators comprising of a dye with a hydrogen bond donating group (-OH or $-NH_2$) and another one with its alkylated group (-OR or $-NR_2$).

The basicity of cyclohexane is defined 0, and the basicity of hexamethylphosphoramide, 1. Normalization schemes for individual indicator pairs were well documented in the literature[2]. Only one research group[16] has reported β values of binary solvents for RPLC including methanol/water mixtures. Their data, however, were based on one pair of indicators, and subject to some uncertainties, thus we redetermined them in this study. β values of mixed solvents for normal phase liquid chromatography were previously measured in our laboratory[18]. In that study, we used only two indicator pairs and suggested that β values of the mixed solvents be reestimated with more indicators. We have redetermined β values of such solvents in this study using totally five indicator pairs.

EXPERIMENTAL

All solvents were HPLC grade from Fisher Scientific Inc. (Pittsburg, PA, U.S.A.) and were used without further purification. The binary solvent mixtures were prepared by mixing a known volume of each liquid, and the composition (ϕ, volume fraction) is defined based on the volume before mixing. The indicator pairs are as follows: the pair of 4-nitrophenol [p-nitrophenol, PNP] and 4-nitroanisole [1], the pair of 4-nitroaniline [14] and N,N-diethyl-4-nitroaniline [6], the pair of 2-nitro-p-toluidine [23] and N,N-dimethyl-o-nitro-p-toluidine [22], the pair of 2-nitroaniline [33] and o-nitrodimethyl aniline [31], and the pair of 2-nitro-p-anisidine [35] and N,N-dimethyl-o-nitro-p-anisidine [34]. The numbers in brackets refer to the Kamlet/Taft indicator designations. Each β determined for an indicator pair is named after the Kamlet/Taft designations. Thus, the five β's based on individual indicator pairs are defined as β_{PNP-1}, β_{14-6}, β_{23-22}, β_{33-31}, β_{35-34}, respectively. The solutes, 22, 31, and 34, were synthesized.

Other chemicals were either kindly donated from professor Peter W. Carr (Department of Chemistry, U of Minnesota, Minneapolis, U.S.A.) or purchased from Aldrich Chemical Co. (Milwakee, WI, U.S.A.) Each solute was tested by HPLC for impurities before spectroscopic measurements, and recrystallized if UV/VIS absorbing impurities existed.

All spectroscopic measurements were carried out by the previously reported procedures[1-5]. A Perkin Elmer UV/VIS double beam spectrophotometer (Model 552S, Perkin Elmer, England) was used to make the measurements to ± 0.2nm with a bandwidth of 1nm. The solute concentration in each mixed solvent is carefully controlled to give absorbance within the range from 0.5 to 1.5. The method of Campbell[19] for synthesis of o-nitro dimethylaniline was extensively modified and applied to syntheses of three indicators 22,31, and 34.

Synthesis of o-Nitrodimethylaniline[31]

A mixture of 10g o-nitrochlorobenzene, 15g sodium bicarbonate, and 80ml pyridine was poured into a 250ml three-neck round bottom flask, then 8g dimethyl hydrochloride dissolved in 3ml warm water was added through a dropping funnel in vigorous agitation. The bottle was heated to the reflux temperature, and the reflux, maintained for 10 hrs. The content was filtered to remove inorganic salts while it was hot, and the filtrate was allowed to evaporate to lose two thirds of its original volume. The crude oily o-nitrodimethyl aniline precipitated upon addition of excess water (ca. 500mL). To the solidified bottom layer (0-5°C) separated from the mother liquid by decantation, 30mL water was added, the temperature, raised to 40°C, and dilute hydrochloric acid, added slowly to give a clear solution, then the pH of the solution was adjusted to pH3. The solution was mixed with 50mL methanol and allowed to stand overnight at 5°C to give needle-like crystal precipitations. The crystals were filtered, dissolved in dilute hydrochloric acid, and recrystallized. The crystals were filtered, dissolved in distilled water, and neutralized to pH7. Pure liquid o-nitrodimethylaniline formed in the bottom was extracted with chloroform. The chloroform solution was washed with distilled water several times, dehydrated in a dessicator, and evaporated to give ca. 4g orange color product. ^{1}H-NMR ($CDCl_3$):δ 2.8 (s, 6H), 6.8-7.7 (m, 4H); MS (EI 30eV): m/z 166 (M , 100), 149 (96.0), 134 (37.2), 121 (68.0), 120 (37.3), 119 (78.0), 118 (80.2), 107 (42.5), 106 (36.4), 105 (73.6), 104 (83.7), 94 (64.3), 92 (69.2), 91 (85.1), 78 (68.1), 77 (77.8); IR (neat): 3090 (w), 2965 (w), 1605, 1564 (s), 1520 (vs), 1477 (s), 1458 (s), 1362 (s), 1348 (s), 1303 (s), 1272 (s), 1120, 1014 (s), 956, 918, 902, 846 (w) cm^{-1}.

Synthesis of N,N-Dimethyl-o-Nitro-p-Toluidine[22]

The procedure was generally similar to that of synthesis of o-nitrodimethylaniline except for use of cyclohexanol instead of pyridine as the reflux solvent since a much higher temperature was required. Dimethylamine hydrochloride was continuously added in a powder form to the dropping funnel and allowed to be washed down by the reflux condensate. An aliquot of cyclohexanol solution was taken for HPLC analysis periodically. The reaction was terminated when the yield reached 90%. We obtained ca. 3g pure cardinal color oily product from 10g N,N-dimethyl-o-nitro-ptoludine. ^{1}H-NMR ($CDCl_3$): δ 2.3 (s, 3H), 2.8 (s, 6H), 6.9-7.5 (m, 3H); MS (EI 30eV): m/z 180 (M^+, 35.1), 163 (35.5), 135 (19.2), 133 (38.3), 132 (27.2), 131 (28.3), 119 (42.4), 118 (58.2), 105 (100), 91 (59.0), 77 (18.1), 69 (49.6), 65 (20.0); IR (neat): 2930, 2905, 2875, 2700 (w), 1619, 1522 (vs), 1448, 1438, 1340 (s), 1278 (s), 1200, 1160, 1149, 1060 (w), 953 (w), 907 (w), 798, 757 (w) cm^{-1}.

Synthesis of N,N-Dimethyl-o-Nitro-p-Anisidine[34]

The procedure was very similar to that of synthesis of N,N-dimethyl-o-nitro-p-toluidine except that the reaction was terminated when the yield reached 75%. We obtained ca. 2g vermilion color oily product from 10g 3-

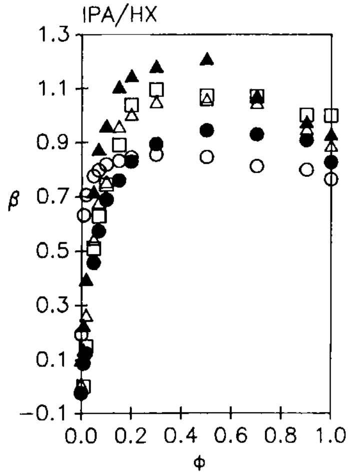

Figure 1. Variation trends of individual β's of 2-propanol/hexane mixtures obtained with 5 indicator pairs with respect to volume fraction of 2-propanol. Symbols; o: β_{PNP-1}, ● : β_{14-6}, Δ:β_{23-22}, ▲ :β_{33-31}, □ : β_{35-34}.

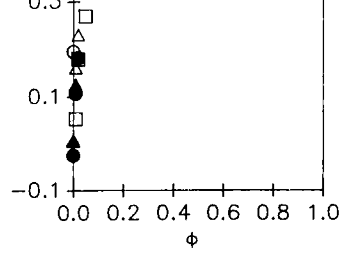

Figure 2. Variation trends of individual β's of ethyl acetate/ hexane mixtures obtained with 5 indicator pairs with respect to volume fraction of ethyl acetate. Symbols; o:β PNP-1, ●: β_{14-6}, Δ : β_{23-22}, ▲ : β_{33-31}, □: β_{35-34}.

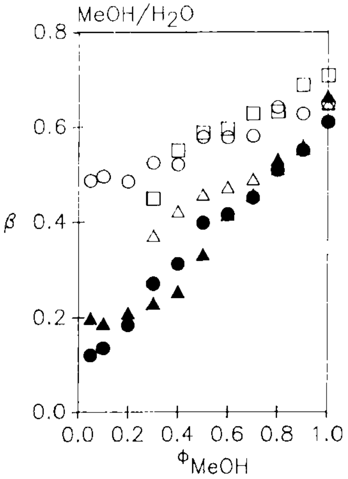

Figure 3. Variation trends of individual β's of methanol/water mixtures obtained with 5 indicator pairs with respect to volume fractin of methanol. Symbols; o: β_{PNP-1}, ● : β_{14-6}, Δ : β_{23-22}, ▲ : β_{33-31}, □ : β_{35-34}.

nitro-4-chloroanisole by following the adequate procedures. ^{1}H-NMR ($CDCl_3$): δ 2.7 (s, 6H), 3.8 (s, 3H), 6.9-7.1 (m, 3H); MS (EI 30eV): m/z 196 (M^+, 53.5), 179 (32.9), 164 (8.0), 151 (34.1), 150 (15.3), 149 (32.2), 135 (77.1), 134 (76.8), 121 (83.7), 120 (100), 106 (27.0), 92 (23.4), 79 (10.0), 77 (18.5); IR (neat): 2920, 2885, 2830, 2795, 1558 (s), 1520 (vs, broad), 1452 (s), 1435 (s), 1323 (s), 1290 (vs,broad), 1237 (s), 1194, 1158, 1142, 1058, 1034 (s), 950 (w), 918 (w), 903 (w), 847 (w), 798 (s), 758 (w), 723 (w), 680 (w) cm^{-1}.

RESULTS AND DISCUSSION

The individual β values obtained with 5 indicator pairs are comparatively plotted with respect to solvent composition in Figure 1 for the 2-propanol/hexane system, in Figure 2 for the ethyl acetate/hexane system, and in Figure 3 for the methanol/water system, respectively. The variation trends of β for the NPLC solvent systems (2-propanol/hexane and ethyl acetate/hexane mixtures) are in a striking contrast to those for the RPLC solvent system (methanol/water mixtures).

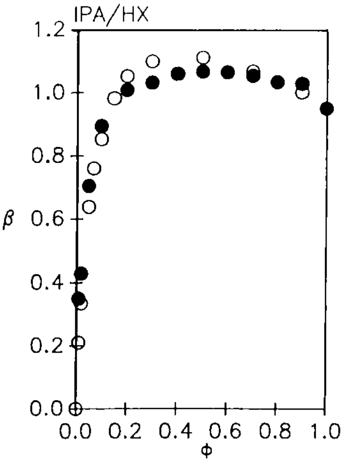

Figure 4. Comparison of the new β values with the previous ones for the 2-propanol/hexane system. Open circle: new values, Closed circle: old values.

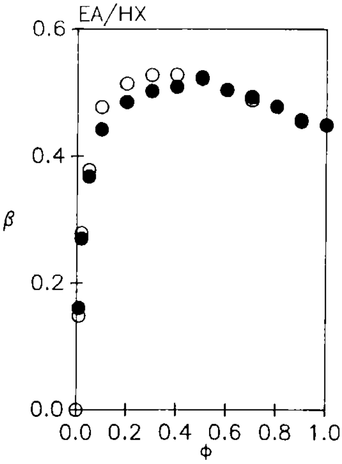

Figure 5. Comparison of the new β values with the previous ones for the ethyl acetate/hexane system. Open circle: new values. Closed circle: old values.

In the 2-propanol/hexane and ethyl acetate/hexane systems, every β follows the same trend; it sharply increases at the beginning, levels off later, reaches a maximum, and decreases as the composition of the more polar solvent varies from 0 to 100%. On the other hand, β's of methanol/water mixtures monotonically increase with methanol content (Figure 3). We observed some scatter for 5 individual β values. The extent of scatter among the 5 data sets remains virtually invariant with respect to solvent composition for the NPLC solvent systems, while the extent of scatter at compositions of lower methanol content (higher water content) tends to be much larger than that at compositions of higher methanol content for the methanol/water system.

There were difficulties in preparing solutions of indicator 22 and 34 in mixed solvents of high water content because of their limited solubilities, and therefore $\beta_{23\text{-}22}$ and $\beta_{35\text{-}34}$ could not be measured for solvents of 0-20% methanol. Nevertheless, $\beta_{23\text{-}22}$ and $\beta_{35\text{-}34}$, tend to fall in the middle of the scatter span of 5 data sets, and the average β values of the 3 data sets for the solvents of 0-20% methanol are regarded to be consistent with the average β values of the 5 data sets for solvents of other compositions.

The averaged (5 data sets) and corrected β values for the 2-propanol/hexane and ethyl acetate/hexane systems are assembled in Table 1. The correction of averaged β values was executed to make the measured β values of mixtures be consistent with the literature βvalues of pure solvents. We obtained β value of 0.027 for pure hexane, 0.880 for pure 2-propanol, and 0.449 for pure ethyl acetate while the literature β values for hexane, 2-propanol, and ethyl acetate are 0, 0.950, and 0.45, respectively. The literature β values are based on much more extended data sets, and are likely to be different from our measured values based on 5 data sets. We believed the literature values are more reliable and made our data be corrected assuming a good linear correlation between the literature and measured β values. Let us define a_1, a_2, as the measured and literature values of pure hexane, b_1, b_2, as the measured and literature values of the pure polar solvent, and x_1, as the measured β value of a mixture, then the corrected β value (x_2) consistent with the literature data is obtained as follows:

$$x_2 = a_2 + \frac{b_2 - a_2}{b_1 - a_1}\left(x_1 - a_1\right)$$

Such correction was not applied to the methanol/water system since we were not able to measure reliable β value of pure water. The measured values

Table 1

The Averaged and Corrected β Values of 2-Propanol/Hexane and Ethyl Acetate/Hexane Mixtures

2-Propanol/Hexane		Ethyl Acetate/Hexane	
ϕ^a	β	ϕ^b	β
0.0	0.0	0.0	0.0
0.01	0.211	0.01	0.149
0.02	0.335	0.02	0.280
0.05	0.638	0.05	0.378
0.07	0.761		
0.1	0.853	0.1	0.478
0.15	0.982	0.2	0.515
0.2	1.052	0.3	0.528
0.3	1.099	0.4	0.529
0.5	1.111	0.5	0.522
0.7	1.067	0.7	0.489
0.9	1.001	0.9	0.455
1.0	0.950	1.0	0.450

a. Volume fraction of 2-propanol
b. Volume fraction of ethyl acetate

of methanol/water mixtures do not seem to be much deviated from the literature values, anyway. The averaged β values for the methanol/water systems are summarized in Table 2.

We mentioned that we had determined β values of 2-propanol/hexane and ethyl acetate/hexane mixtures using only 2 indicator pairs in the previous study[18]. We compared the new β values with the previous ones in Figure 4 (2-propanol/hexane mixtures) and in Figure 5 (ethyl acetate/hexane mixtures). Assuming that the new data based on 5 indicator pairs are more reliable than the old data based on 2 indicator pairs, we noted that the old β values are a little overestimated at lower content of the more polar solvent and that the values around the maximum are more or less underestimated (See Figures 4 and 5).

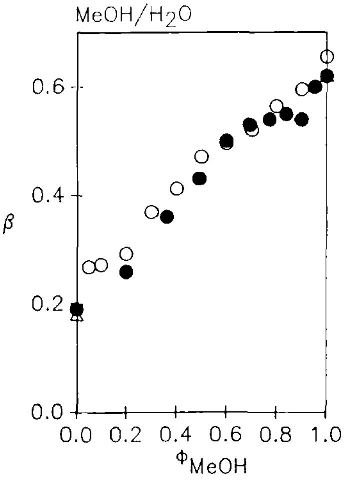

Figure 6. Comparison of the new βvalues with the previously reported ones. Open circle: new values, Closed circle: old values, Open triangle: the original literature value for pure solvents.

Table 2

The Averaged β Values of Methanol/Water Mixtures

ϕ^a	β^b
0.05	0.269 (0.193)
0.1	0.273 (0.195)
0.2	0.293 (0.166)
0.3	0.369 (0.122)
0.4	0.412 (0.128)
0.5	0.470 (0.112)
0.6	0.495 (0.077)
0.7	0.521 (0.071)
0.8	0.564 (0.059)
0.9	0.596 (0.054)
1.0	0.656 (0.032)

---

a. Volume fraction of methanol

b. Standard deviations are given in parentheses

We also mentioned that a research group had reported β values of methanol/water mixtures using only one indicator pair[16]. The newly determined and previously reported values are compared in Figure 6. They are roughly identical but the irregular fluctuation present in the plot of old data disappears in the plot of new data. We can note that the β of methanol/water mixtures are almost linearly correlated with volume fraction of methanol.

We believe that the appearance of a maximum in the plot of β against solvent composition for the 2-propanol/hexane and ethyl acetate/hexane systems is real considering that all of the five data sets show exactly the same trend. We now turn to rationalizing how a mixture of two solvents can have higher basicity than either of the pure solvents does. Appearance of extrema in plots of polarity scales of mixed solvents vs. solvent composition is occasionally observed when the system is composed of a polar and a nonpolar solvents[20-22]. We first emphasize that all indicator dyes used in solvatochromic measurements are moderately polar in general[1-5].

We should also note that a polarity scale of a solvent , whether pure or mixed, is monitored by an indicator, and that the polarity determined by the indicator actually refers to the local environments around the indicator. It is very likely that the environments of an indicator get more polar as the polar solvent is added to the pure nonpolar solvent, and it actually happens at the initial stage of addition. The more polar solvent molecules seem to behave in two different fashions when the more polar solvent is introduced into the nonpolar solvent. First, they coordinate the indicator molecules to give strong solute-solvent interactions. Second, they coordinate themselves one another to yield strong solvent-solvent interactions forming dimeric or polymeric aggregates. In the latter case, strong functional groups interact one another inside the aggregates, then the aggregates will not be capable of strong solute-solvent interactions, which leads to reduction of solvent polarity. The former process prevails when the composition of more polar solvent is low since formation of aggregates of polar solvent molecules is thermodynamically forbidden (very high negative entropy change).

The free monomeric polar solvent molecules selectively coordinate solute molecules, and addition of a small amount of the polar solvent to the nonpolar solvent causes a sharp increase of polarity as is shown in Figures 4 and 5. As the more polar solvent is further added, the second process gets more favorable, thus the basicity of the mixed solvent reaches a maximum and reduces after the composition pass the limit where the number density of monomeric polar solvent molecules hits its maximum. Hurtubise et al.[17] proposed similar arguments in their sovatochromic study for 2-propanol/heptane and ethyl acetate/ heptane mixtures. They noted that there were two major hydrogen bondings- a region where monomeric hydrogen-bonding solvent molecules were interacting with the solute molecules, and a region where dimeric or polymeric hydrogen-bonding solvent molecules were interacting with the solute molecules.

On the other hand, β monotonically and linearly varies with respect to methanol composition for the RPLC solvent system (methanol/water). We can expect a similar variation trend to those of the NPLC solvent systems if we merely consider that there is large difference in β between water (0.18) and methanol (0.62). We suggest a very crude and qualitative explanation to account for the linear variation of β with ϕ for methanol/water mixtures. Not difference in β but difference in the overall molecular polarity contributes to formation of dimeric or polymeric aggregates of the more polar solvent. Considering that π^* (dipolarity/ polarizability, 1.09) of water is greater than π^* (0.60) of methanol, α (hydrogen bond donating acidity, 1.17) of water, a little greater than α (0.93) of methanol, and β (0.18) of water, smaller than β (0.62) of methanol, we may conclude that the overall polarity of water is roughly comparable to that of methanol.

This argument is against the general conception that water is much more polar than methanol as we note that addition of water to pure methanol yields a striking increase in solute retention in RPLC and that nonpolar solutes do not dissolve in water but moderately dissolve in methanol. But the peculiar polarity of water in phase-transfer-related processes is largerly due to the very high cohesive energy density of water which causes a very high positive cavity formation energy when a solute is introduced in water. When only molecular interactions are considered, as in solvatochromic measurements, the overall polarity of water could be regarded to be roughly similar to that of methanol. In such a situation, both methanol and water will not form aggregates of one kind but yield random and uniform mixing. Therefore β of the mixture linearly correlates with volume fraction of methanol.

It is interesting to note that Katz et al.[23] proposed that a mixtures of water and methanol is composed of three species, that is, water, methanol, and 1:1 complex of water and methanol. Their view also seems to support random and uniform mixing. Cheong et al.[24] reported a possibility of existence of a minimum in the plot of α (hydrogen bond donating acidity) of aqueous methanol mixtures vs. methanol volume fraction based on solvatochromatic data obtained with a zwitterion type betaine dye, which might support nonrandom mixing between water and methanol, but later Park et al.[25] showed that use of a non-zwitterion type indicator free of specific interactions yielded a monotonous variation of α with respect to methanol volume fraction. There have been some reports that allude similarity in polarity (excluding cohesive energy density effect) between water and methanol. Some workers[26-27] observed a linear trend in plots of ln k' vs. methanol volume fraction. A linear relationship of the logarithmic solute activity coefficient in aqueous methanol mixtures with methanol volume fraction was also observed[28]. Street et al.[29] obtained a linear correlation between Py (solvatochromic polarity scale based on light absorption of pyrene) and methanol volume fraction. Krygowski et al[16]. and Johnson et al.[30] showed an almost linear correlation between E_T (solvatochromic polarity scale based on a betaine dye) and methanol volume fraction. On the other hand, in other RPLC solvent systems such as acetonitrile/water, 2-propanol/water, or tetrahydrofuran/water, nonlinear relationships were observed between a solvatochromatic or chromatographic/ thermodynamic property and ϕ.[16,26-30]

CONCLUSIONS

The appearance of a maximum in the plots of β vs. solvent composition for NPLC solvent systems seems to be related to the twofold behaviors of the more polar solvent molecules: formation of solute-solvent interactions (monomeric solvent) and aggregation of solvent molecules (polymeric solvent). The averaged and corrected β data reported in this study could be useful for LSER applications in liquid chromatography. The linear correlation of β with volume fraction of methanol for the methanol/water system leads to the conclusion that either water or methanol molecules do not form polymeric aggregates of one kind but randomly mix with the other solvent molecules.

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