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SOLUBILITY PARAMETER AND WINDOW DIAGRAM OPTIMIZATION METHODS FOR THE REVERSED-PHASE CHROMATOGRAPHIC OPTIMIZATION OF COMPLEX HYDROXYL AROMATIC MIXTURES

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SUMMARY

The solubility parameter and window diagram optimization methods were compared for optimizing ternary mobile phases for the reversed-phase liquid chromatographic separation of complex aromatic mixtures. The study revealed that the solubility parameter method predicted a much better optimum mobile phase composition for a monohydroxyl mixture. Also, the solubility parameter method predicted a better optimum mobile phase for a dihydroxyl mixture. However, the window diagram method gave two optima, and one of the optima was identical to the optimum obtained by the solubility parameter approach. It was also found that the solubility parameter method reduced uncertainties for secondary mobile phase optima. The differences obtained with the two methods can be attributed to the dissimilarity of the optimization criterion used in each method.

INTRODUCTION

One of the primary objectives in the development of high-performance liquid chromatography (HPLC) separations is the optimization of mobile phase selectivity. This is particularly important in the development of separation methods for highly complex mixtures which necessitate the resolution of as many components as possible. Often, the main concern is not the time required to obtain the separation, but rather the selectivity achieved by the separation[1,2]. However, a constraint on separation time becomes extremely important when the peak capacity of a column is considered for a multi-component chromatogram[3,4].

The optimization of mobile phase selectivity requires the adjustment of the mobile phase composition. In the past, this was done by trial and error. However, there are now several methods available for the systematic optimization of mobile phase selectivity. In general, these optimization methods are based on models for predicting retention behavior[5–14] or use statistical or sequential search techniques[15–20].

Our previous work showed that the solubility parameter optimization method developed by Schoenmakers *et al.*[11] and Drouen *et al.*[12] provided a systematic method for determining optimal mobile phase conditions for highly complex hydroxyl aromatic mixtures[21]. In this work, the complex hydroxyl aromatic mixtures investigated earlier[21] were subjected to a different systematic optimization method based on window diagrams[5–7]. In addition, this work presents the first detailed comparison of the window diagram[5–7] and solubility parameter optimization methods[11,12]. Results showed that the window diagram method was inferior to the solubility parameter approach for predicting optimal mobile phase conditions and minimized ambiguities for secondary mobile phase optima for highly complex hydroxyl aromatic mixtures.

EXPERIMENTAL

High-performance liquid chromatograph

The liquid chromatograph used was a Waters Model ALC-GPC 244 equipped with a Model 6000A pump, a Model M-45 pump, both controlled by a Model 680 automated gradient controller for operation in the isocratic or gradient modes. A U6K injector, a dual-channel free-standing ultraviolet detector set at 254 nm and 280 nm, a Bascom-Turner Model 8120 electronic recorder, a dual-channel 10-mV strip chart recorder, and a Hewlett-Packard 3390 A integrator were also used.

Columns

The columns employed were a 30 cm × 3.9 mm I.D. pre-packed C_{18} column obtained from Waters Assoc., Milford, MA, U.S.A. and a 25 cm × 4.6 mm I.D. pre-packed C_8 column obtained from Fisher Scientific, Pittsburgh, PA, U.S.A. The Waters column was packed with μBondapak C_{18} and consisted of octadecyl groups chemically bonded to Waters 10-μm porous silica. The Fisher column was packed with Resolvex C_8 and consisted of octylsilane groups chemically bonded to Fisher Resolvex Sil (10-μm porous silica).

Reagents

HPLC-grade methanol, acetonitrile, and tetrahydrofuran were obtained from Fisher Scientific and were prefiltered through a Millipore type FH 0.5-μm filter. Distilled water was prefiltered through a Millipore Milli-Q water purification system obtained from Millipore, Bedford, MA, U.S.A. Binary and ternary solvent mixtures were degassed by stirring overnight. The hydroxyl aromatic standards were obtained from commercially available sources and were purified when necessary.

Procedures

Details of the experimental procedures and chromatographic systems were described elsewhere[21].

RESULTS AND DISCUSSION

Theoretical considerations

The window diagram optimization method was originally developed for optimizing stationary phases in gas–liquid chromatography[5]. Recently, however, the window diagram approach has been used to optimize mobile phase selectivity in HPLC[7,14,22,23].

The window diagram method is a graphical method for depicting chromatographic retention data. Optimal conditions are determined by maximizing the selectivity (α) of the most difficult to resolve peak pairs as a function of one or more experimental variables. Originally, the optimizing criterion was defined as the relative retention

$$\alpha_{i,j} = \frac{V_i - V_0}{V_j - V_0} \tag{1}$$

where V_i and V_j are retention volumes of solutes i and j, respectively, and V_0 is the column void volume[5]. However, Jones and Wellington[24] have shown that the optimization criterion, α, can lead to inaccurate window diagrams when V_0 is not much smaller than V_i and V_j. Therefore, they defined the optimization criterion, S, which does not require the measurement of V_0. The separation factor, S, is defined by eqn. 2[24].

$$S = \frac{V_i - V_j}{V_i + V_j} \tag{2}$$

Jones and Wellington[24] and Hsu *et al.*[7] have shown that α and S delineate equivalent window diagrams providing V_0 is not similar to solute retention volumes. In addition, Hsu *et al.*[7] have shown that window diagrams constructed using chromatographic resolution, R_s, α and S necessarily coincide when solute capacity factors approach 10 or more.

Schoenmakers *et al.*[11] and Drouen *et al.*[12] have developed a systematic optimization method based on solubility parameter theory. The criteria for optimization are based on the fundamental equation of resolution which can be defined in one form as

$$R_{s_{i,j}} = \frac{\sqrt{N}}{2}\left(\frac{k_i - k_j}{k_i + k_j + 2}\right) \tag{3}$$

where k_i and k_j are capacity factors for solutes i and j and N is the plate number of the column. Neglecting constant factors ($\sqrt{N}/2$), Schoenmakers *et al.*[11] have proposed the optimization criterion, ΠR_s, defined as the product of resolution factors, $(k_{i+1} - k_i)/(k_{i+1} + k_i + 2)$, for each pair of adjacent peaks in a chromatogram.

$$\Pi R_s = \prod_{i=1}^{n-1} \frac{k_{i+1} - k_i}{k_{i+1} + k_i + 2} \tag{4}$$

Drouen *et al.*[12] have modified the above criterion to take into account changing chromatogram length with changes in solvent composition. Hence, they defined, r, the relative product which proved to be more important than ΠR_s[12].

$$r = \prod_{i=1}^{n-1} R_{s_{i+1,i}} \Big/ \left[\left(\sum_{i=1}^{n-1} R_{s_{i+1,i}}\right) \Big/ (n-1)\right]^{n-1} \tag{5}$$

Optimal mobile phase conditions correspond to maximizing r. However, it is important to retain the criterion, ΠR_s, throughout the optimization since a maximum value of the criterion, r, does not necessarily imply an optimum separation[12].

Interestingly, it can be shown easily that the separation factor, S, (eqn.2) is proportional to R_s (eqn. 3)[24]. Therefore, S is proportional to ΠR_s (eqn. 4). Moreover, R_s is independent of column void volume which necessitates that S, ΠR_s and subsequently r (eqn. 5) are also independent of V_0. Therefore, the only difference between the optimization criterion S and the ΠR_s expression is that the latter corresponds to the product of resolution factors, or S values, for each adjacent peak pair in a chromatogram. This provides a convenient means of directly comparing the optimization criteria utilized in the window diagram[5–7] and solubility parameter[11,12] optimization methods.

General considerations

Mobile phase optimization using the window diagram or solubility parameter methods requires that two conditions be satisfied. First, one must be able to identify individual solutes in a mixture for a given chromatogram. In our previous work[21] and in this study, identification was accomplished on the basis of individual solute retention volumes. Secondly, one must be able to predict changes in solute capacity factors as a function of mobile phase composition or some other experimental variable. This premise requires the measurement of column void volume, a condition not required in calculating values of the optimization criteria S, ΠR_s and r. In our earlier work[21], it was assumed that log k' varied linearly with the composition of ternary mixtures formed by mixing two iso-eluotropic mobile phases[11,12]. However, deviations from the assumed linear relationships are expected and are experimentally observed due to specific solute-solvent effects[25]. The non-linear behavior of log k' as a function of mobile phase composition was accounted for earlier[21] using the iterative routine developed by Drouen *et al.*[12] to efficiently ascertain optimal mobile phase conditions. The goal of this work was to directly compare the window diagram and solubility parameter optimization methods. Therefore, the chromatographic retention data generated in our previous work[21] were used to construct window diagrams for complex mono- and dihydroxyl aromatic mixtures from which optimal mobile phase conditions could be predicted. In addition, it was assumed that log k' varied linearly between each consecutive mobile phase composition range used in constructing the window diagrams, although, the slopes of the lines for each consecutive mobile composition range were not necessarily the same. This assumption was utilized in our previous optimization effort[21] and is an integral part of the solubility parameter optimization method[11,12].

Mobile phase optimization for monohydroxyl aromatic compounds

Twenty-one monohydroxyl aromatic compounds were investigated earlier with a reversed-phase column using several binary and ternary iso-eluotropic mobile phases[21]. The retention data obtained for the monohydroxyl aromatics with methanol–water, tetrahydrofuran (THF)–water, and acetonitrile–water iso-eluotropic binary mobile phases were published earlier[21]. Table I gives the monohydroxyl aromatic compounds investigated and the chromatographic data obtained with the iso-eluotropic ternary mobile phases. Using the data from the iso-eluotropic binary mobile

TABLE I

LOG k' VALUES FOR MONOHYDROXYL AROMATICS ON μBONDAPAK C_{18} WITH ISO-ELUOTROPIC TERNARY MOBILE PHASES

Compound		*Acetonitrile–THF–water*		
		9.4:32.5:58.1	*14.6:28.3:57.1*	*19.2:24.7:56.1*
1	1-Acenaphthenol	0.15	0.14	0.13
2	5H-Dibenzo[*a*,*d*]cycloheptene-5-ol	0.53	0.53	0.50
3	7,12-Dimethyl-9-hydroxybenz[*a*]-anthracene	0.85	0.91	0.91
4	2-Hydroxybenzo[*c*]phenanthrene	0.71	0.75	0.77
5	3-Hydroxybenzo[*c*]phenanthrene	0.68	0.72	0.74
6	1-(1-Hydroxymethyl)pyrene	0.51	0.54	0.55
7	1-(Hydroxymethyl)benz[*a*]pyrene	0.59	0.66	0.68
8	4-Hydroxymethylpyrene	0.40	0.43	0.43
9	9-Hydroxyphenanthrene	0.61	0.62	0.61
10	13-Hydroxypicene	1.03	1.11	1.14
11	1-Hydroxypyrene	0.65	0.69	0.68
12	4-Hydroxypyrene	0.64	0.68	0.69
13	1-Indanol	−0.07	−0.11	−0.12
14	5-Indanol	0.33	0.31	0.27
15	1-Naphthol	0.39	0.38	0.35
16	2-Naphthol	0.31	0.29	0.26
17	3-Phenylphenol	0.47	0.47	0.44
18	1,2,3,4-Tetrahydro-4-hydroxy-4-methylphenanthrene	0.60	0.60	0.58
19	1,2,3,4-Tetrahydro-1-naphthol	0.08	0.06	0.03
20	5,6,7,8-Tetrahydro-1-naphthol	0.50	0.49	0.46
21	5,6,7,8-Tetrahydro-2-phenanthrol	0.69	0.72	0.69

phases and the data in Table I, it was determined that the optimal mobile phase for the separation of the complex monohydroxyl aromatic mixture on μBondapak C_{18} and on Resolvex C_8 was acetonitrile–THF–water (15.2:27.8:57.0)[21]. Therefore, using the pertinent retention data from ref. 21 and Table I a window diagram was con-

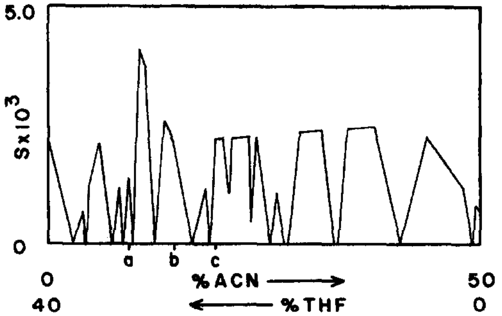

Fig. 1. Window diagram for 21 monohydroxyl aromatic compounds calculated from the data in ref. 21 and Table I. Optimum composition is predicted to be acetonitrile–THF–water (10.3:31.7:58.0). Lines that did not define a window have been omitted for clarity. The letters a, b and c correspond to the compositions acetonitrile–THF–water (9.4:32.5:58.1, 14.6:28.3:57.1 and 19.2:24.7:56.1, respectively) (see Table I). ACN = Acetonitrile.

structed for the acetonitrile–THF–water ternary system. Fig. 1 shows the computer generated window diagram for the acetonitrile–THF–water ternary system assuming a linear interpolation between consecutive mobile phase composition ranges. Peak crossovers ($\alpha < 1$; S and $R_s < 0$) are handled in the computer program by taking the reciprocal, so that the plotted line is always above the x-axis where $\alpha = 1$ or S and $R_s = 0$. In addition, the computer program considers all possible peak pairs at each mobile phase composition in generating the window diagrams. The window diagram in Fig. 1 was obtained by plotting the separation factor, S, as a function of mobile phase composition. However, identical window diagrams were obtained when α or R_s were plotted on the ordinate. Thus, it was concluded that the determination of the column void volume was a good estimate since the window diagram plotted using α was equivalent to Fig. 1. Hsu *et al.*[7] have observed similar results.

The window diagram in Fig. 1 predicts an optimum mobile phase composition of 10.3:31.7:58.0 (acetonitrile–THF–water) for the separation of the complex monohydroxyl aromatic mixture. In contrast, it was shown earlier that the solubility parameter mobile phase optimization method predicted an optimum composition of 15.2:27.8:57.0 (acetonitrile–THF–water). Fig. 2 shows the chromatogram obtained for the separation of the complex monohydroxyl aromatic mixture using the predicted optimum from Fig. 1. Likewise, Fig. 3 shows the chromatogram obtained using the predicted optimum obtained previously[21]. Comparison of Figs. 2 and 3 reveals that a much better separation is achieved using the optimum predicted using the solubility parameter optimization method[21]. Fig. 3 shows seventeen discernable

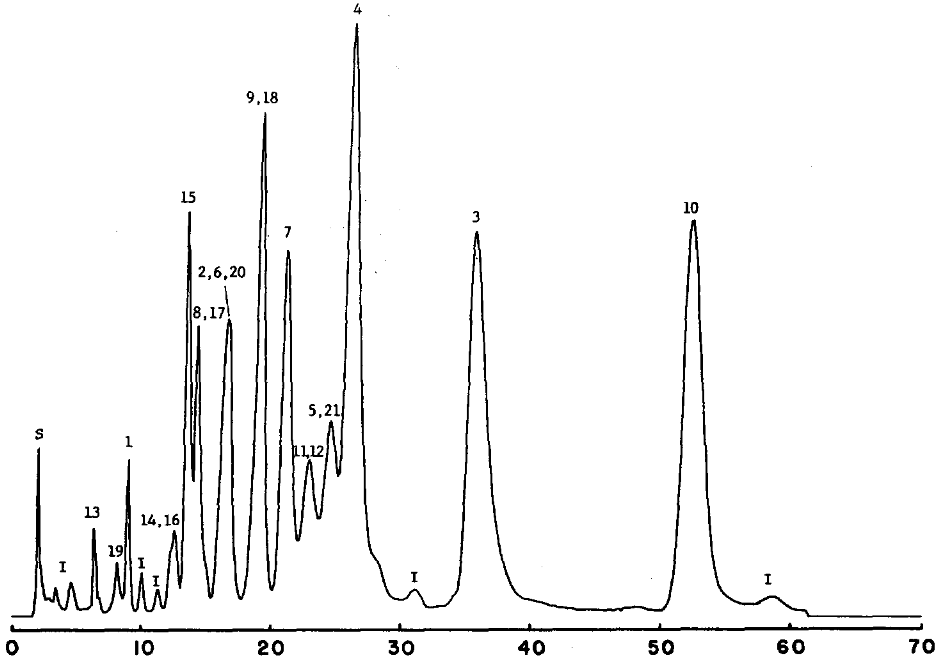

Fig. 2. Chromatogram of monohydroxyl aromatic mixture obtained on Resolvex C_8 using the optimum mobile phase predicted in Fig. 1. S and I refer to solvent and impurity peaks, respectively.

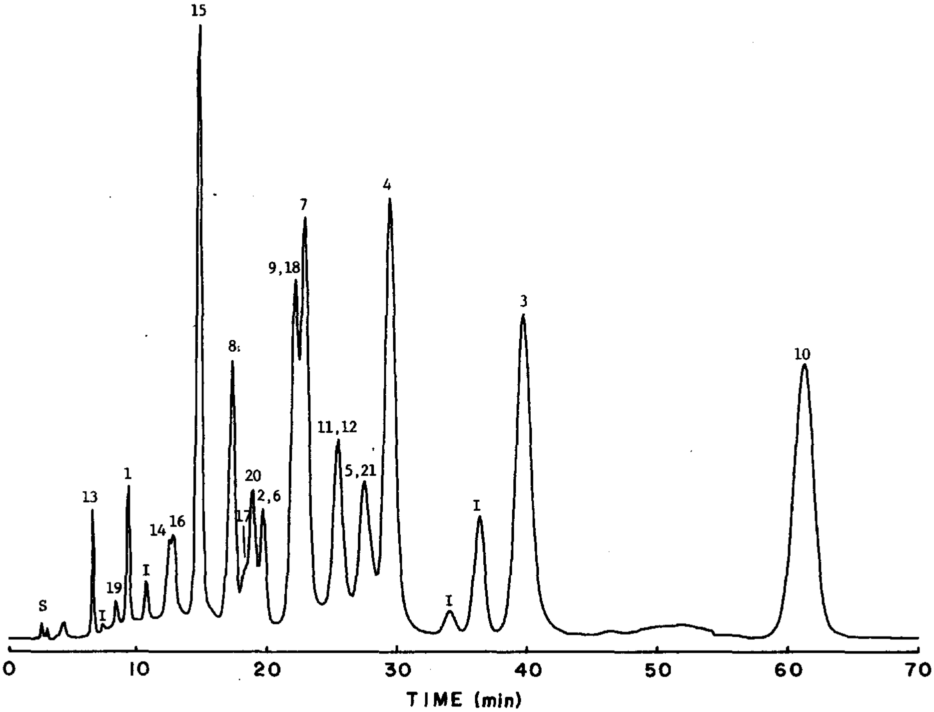

Fig. 3. Chromatogram of monohydroxyl aromatic mixture obtained using the optimum mobile phase acetonitrile–THF–water (15.2:27.8:57.0) on Resolvex C_8 from ref. 21. S and I refer to solvent and impurity peaks, respectively.

peaks compared to the fourteen peaks evident in the chromatogram in Fig. 2. Therefore, it is apparent that the window diagram in Fig. 1, constructed using the same retention data and assumptions as in our previous work[21], does not predict the global optimum for the monohydroxyl aromatics. Generally, it has been professed that the window diagram method locates the global optimum based on the most difficult to resolve peak pairs[5–7]. However, in this case, it is not satisfactory to predict an optimum composition based primarily on one pair of peaks at the expense of all other peaks in a complex chromatogram. Rather, all peak pairs must be considered in the optimization criterion as is done in the solubility parameter optimization method. In fact, this is the only difference between the criteria S and ΠR_s (eqns. 2 and 4) and is apparently reflected by the better separation shown in Fig. 3 compared to Fig. 2. Other factors which may be contributing to the different predicted optimum compositions include errors in the calculated capacity factors and the need for additional retention data to construct a more accurate window diagram. At this time, it is not clear what impact if any these factors have on the window diagram optimization method. Additional work is needed to fully ascertain the relevance of these factors on the window diagram method for predicting optimum ternary mobile phases because very little work has been done in constructing window diagrams from ternary mobile phase retention data.

Mobile phase optimization for dihydroxyl aromatic compounds

Similar to the previous discussion, the separation of a mixture of fourteen dihydroxyl aromatic compounds was optimized on a reversed-phase system with the solubility parameter approach[21]. Optimal mobile phase conditions were determined to be 8.5:19.7:71.8 (methanol–THF–water) for separating the complex dihydroxyl aromatic mixture[21]. The chromatogram for the separation of the dihydroxyl aromatics with the above ternary mobile phase is shown in Fig. 4. Fig. 5 shows the resultant window diagram for the methanol–THF–water ternary system obtained using the pertinent data in ref. 21 and Table II. The window diagram in Fig. 5 shows two windows with nearly equivalent maximum S values. The primary window, the window with the largest S value, predicts an optimum of 38.5:1.0:60.5 (methanol–THF–water), whereas the secondary window, labelled "b" in Fig. 5, predicts an optimum of 8.5:19.7:71.8 (methanol–THF–water) for the separation of the dihydroxyl aromatics. In general, the primary criterion used in the window diagram method for predicting optimal conditions is the window denoted by the maximum value of α, R_s or S^{5-7}. Fig. 6 shows the chromatogram obtained using the mobile phase composition predicted by the primary window in Fig. 5.

Comparison of the chromatograms in Figs. 4 and 6 shows that Fig. 4 exhibits eleven discernable peaks compared to ten for Fig. 6. Also, the chromatogram in Fig. 4 clearly shows better overall resolution and selectivity. Thus, as in the previous discussion the window diagram optimization method predicts an inferior optimal

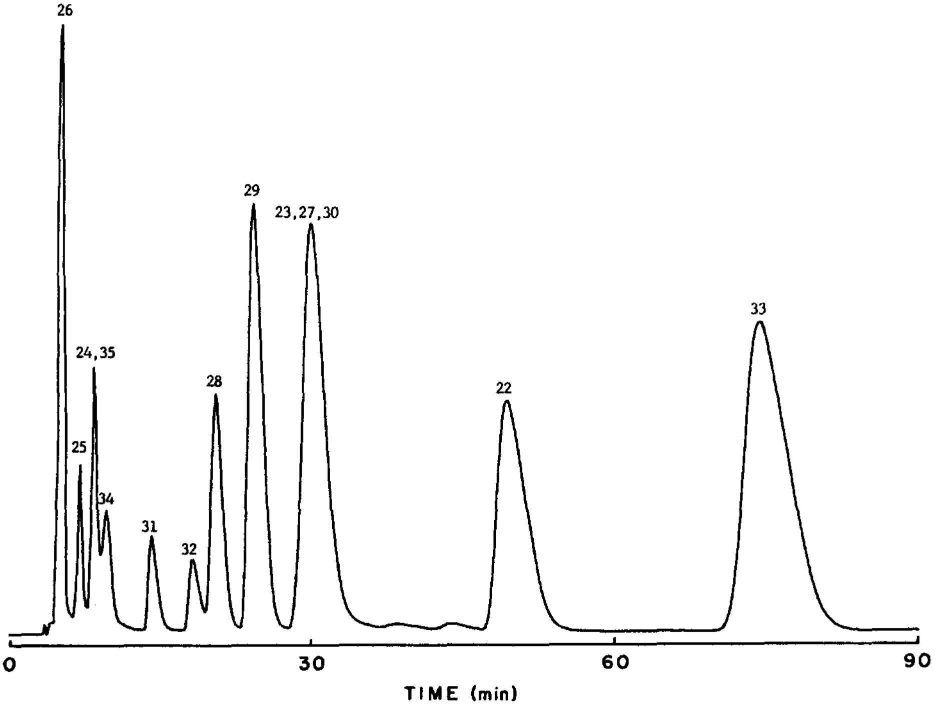

Fig. 4. Chromatogram of dihydroxyl aromatic mixture obtained using the optimum mobile phase methanol–THF–water (8.5:19.7:71.8) on μBondapak C_{18} from ref. 21.

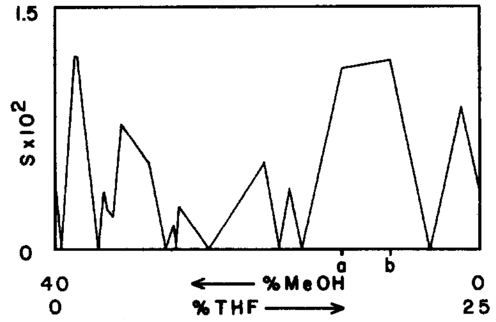

Fig. 5. Window diagram for 14 dihydroxyl aromatic compounds calculated from the data in ref. 21 and Table II. Optimum composition is predicted to be methanol–THF–water (38.5:1.0:60.5). Lines that did not define a window have been omitted for clarity. The letters a and b correspond to the compositions methanol–THF–water (13.1:16.8:70.1 and 8.5:19.7:71.8, respectively) (see Table II). MeOH = Methanol.

mobile phase composition compared to the solubility parameter optimization method. However, on the basis of Fig. 5 the mobile phase composition predicted by the secondary window, 8.5:19.7:71.8 (methanol–THF–water), cannot be ignored. In fact, this composition is identical to the optimum composition predicted earlier by the solubility parameter method for the dihydroxyl aromatic mixture[21]. Therefore, in this case, the two optimization methods predict equivalent mobile phase conditions if the secondary window is considered. This result may be attributable to the simpler mixture investigated for the dihydroxyl mixture. Clearly, the same results were not evident for the monohydroxyl aromatic mixture discussed previously. Furthermore, the window diagram shown in Fig. 5 exemplifies the problem of secondary optima. Both the window diagram and solubility parameter methods give multiple optima due to numerous peak crossovers. However, the solubility parameter method based

TABLE II

LOG k' VALUES FOR DIHYDROXYL AROMATICS ON μBONDAPAK C_{18} WITH ISOELUTROPIC TERNARY MOBILE PHASES

Compound		*Methanol–THF–water*	
		18.5:19.7:71.8	*13.1:16.8:70.1*
22	*o,o'*-Biphenol	1.21	1.19
23	*p,p'*-Biphenol	0.96	0.95
24	1,2-Dihydroxybenzene	0.29	0.24
25	1,3-Dihydroxybenzene	0.15	0.10
26	1,4-Dihydroxybenzene	−0.18	−0.18
27	1,3-Dihydroxynaphthalene	0.99	0.97
28	1,6-Dihydroxynaphthalene	0.79	0.74
29	1,7-Dihydroxynaphthalene	0.91	0.84
30	2,3-Dihydroxynaphthalene	0.98	0.96
31	2,6-Dihydroxynaphthalene	0.60	0.54
32	2,7-Dihydroxynaphthalene	0.74	0.68
33	2,5-Dihydroxynaphthalene	1.41	1.40
34	2,6-Dihydroxytoluene	0.36	0.22
35	3,5-Dihydroxytoluene	0.31	0.26

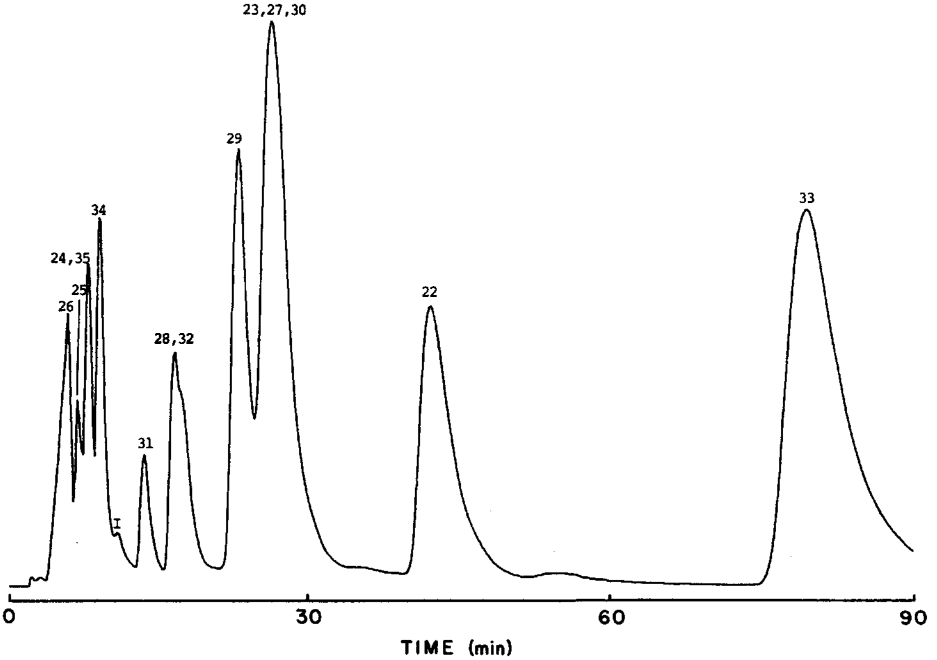

Fig. 6. Chromatogram of dihydroxyl aromatic mixture obtained on μBondapak C_{18} using the predicted optimum mobile phase in Fig. 5. I refers to impurity.

on our results[21], reduced the ambiguity of secondary optima in contrast to the window diagram results presented in this work. Namely, only one primary optimum was obtained with the solubility parameter approach[21].

Undoubtedly, the solubility parameter method predicted the better optimal mobile phase conditions compared to the window diagram method for the monohydroxyl aromatic mixture. In addition, the solubility parameter method reduced secondary optima uncertainty in contrast to the window diagram method for the dihydroxyl mixture. It appears that the fundamental reason for the observed differences between the two optimization methods can be attributed to the criterion used to predict optimal mobile phase conditions. The window diagram method predicts optimal conditions based upon the most difficult to resolve peak pairs, whereas the solubility parameter optimization method takes into account all peak pairs in predicting optimal conditions. In fact, the S values from the window diagrams for all adjacent peak pairs in a chromatogram can be used to construct the identical mobile phase selection diagrams obtained with the criterion ΠR_s discussed earlier[21]. We accomplished this for both the mono- and dihydroxyl aromatics by calculating the product of all S values in the window diagram as a function of mobile phase composition and plotting the results. The mobile phase selection diagrams necessarily resulted because ΠR_s (eqn. 4) is equal to the product of S values (eqn. 2) for adjacent chromatographic peaks. Indeed, the window diagram method has been used successfully in the past to predict optimal conditions; however, based on the results reported in this work, the better optimum for complex mixtures is predicted utilizing all peak pairs in a complex mixture. In this work, the criteria πR_s and r apparently define the global optimum and reduce secondary optima problems contrary to the criteria α, S and R_s. Finally, the solubility parameter optimization criteria πR_s[11] and r[12] do not give unmanageable responses when peak crossover occurs contrary to previous conclusions[26]. Our earlier work showed that definite maximum values of the criteria were obtained which were clearly much larger than any of the secondary optima[21].

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