

Influence of Added Electrolyte to the Stationary Phase on Retention and Selectivity in Gas-Liquid Chromatography

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Recently, we have determined adsorption and partition coefficients for 26 nonelectrolytes measured by gas chromatography on aqueous NaCl columns containing electrolyte at concentrations up to 5.3 molal (1). While the primary purpose of this research was to study the effect of the addition of electrolyte on the gas-liquid interfacial adsorption of sparingly soluble nonelectrolytes on electrolyte solutions by gas-liquid chromatography (GLC), the results also are of interest in analytical chromatographic separations. We should like to report here a portion of this research which has important consequences in several areas of chromatographic research. Namely, these are: 1) The effect of electrolyte addition to the stationary phase in gas chromatography on the net retention volume of various solutes. 2) The change in the relative retention for various solute pairs which are retained on the column by singular and dual retention mechanisms upon addition of electrolyte to the stationary phase. 3) With respect to (1) and (2), to note the effect of the solute interfacial adsorption at the gas-liquid

interface on the determination of bulk solution retention constants and complexation constants.

It is well established that retention of solutes in gas-liquid chromatography columns may be represented by a summation of discrete retention volumes for the various retention modes operative in the column. For a binary solute retention mechanism consisting of adsorption at the gas-liquid interface and partition into the bulk stationary phase, the net retention volume per gram of packing, V_N° , is given as

$$V_N^\circ = K_A A_L^\circ + K_L V_L^\circ \quad (1)$$

where K_A = adsorption coefficient of the solute at the gas-liquid interface. A_L° = surface area of the gas-liquid interface per gram of packing. K_L = partition coefficient of the solute in the bulk stationary phase. V_L° = volume of the stationary phase per gram of packing.

The presence of a dual retention mechanism described in Equation 1 can readily be shown by noting the change in

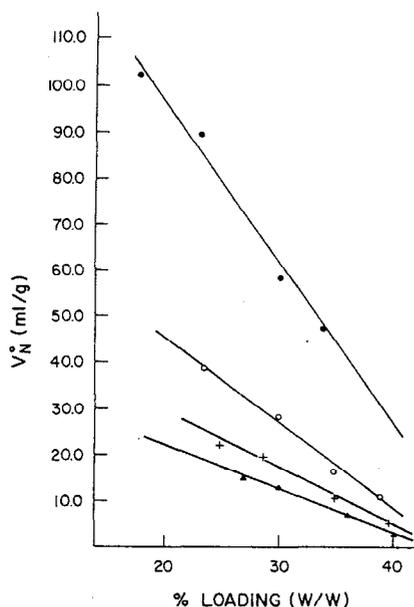


Figure 1. V_N^0 vs. % loading for *n*-nonane on the following stationary phases. (\blacktriangle) 0.54*m* NaCl, (+) 1.13*m* NaCl, (O) 2.34*m* NaCl, (\bullet) 5.34*m* NaCl, temp. = 12.5 °C

the net retention volume as a function of stationary phase loading, i.e., the change in the surface area/volume ratio of the stationary phase.

The above equation is valid provided that there is no effect on solute retention due to Kelvin retention (2). Calculations for the solutes and salt solutions in this study indicate that Kelvin retention is negligible, a fact that is not surprising in view of limited solubility exhibited by the solutes in the salt solutions used for this study.

EXPERIMENTAL

The basic experimental apparatus and procedure have been described elsewhere (1, 3, 4). Porasil D (Waters Associates, Framingham, MA) was used as a solid support. Ultra pure NaCl (Ventron Chemical Corp., Beverly, MA) was employed in the preparation of the salt solutions, after heating at 400 °C for a period of 48 hours.

The solutes selected for this study consisted largely of compounds for which adsorption and partition coefficient data had been previously determined on pure water columns (3-5). All solutes used in this study were reagent grade chemicals and used without further purification. The source of these solutes are listed in Ref. (1).

Preparation of the aqueous salt solutions on Porasil D was accomplished by the rotary evaporation technique used previously. Initially, a standard NaCl solution was prepared, from which a precisely-titrated amount was added to a known weight of silica beads. An excess of water was then added to form a slurry from which the required amount of water was then removed to yield the desired coating weight and electrolyte concentration.

Gravimetric assay of the column packing was performed twice; once with an aliquot of the packing before the column was filled, and again after the experiment, by emptying the column contents for analysis. Initial drying gave the amount of water on the column, while subsequent washing with water and drying yielded the weight of NaCl in solution. The precision of this method of assay was checked and found to be 1.5 parts per thousand.

At each electrolyte concentration, several columns of different w/w% loadings were required to ascertain both K_L and K_A . From an experimental point of view, this required reproducing the same NaCl concentration at several w/w% loadings. Despite this twofold requirement, the rotary evaporation technique was successfully employed for this purpose as evidenced by the following ionic concentrations and their standard deviations: 0.25 ± 0.01*m*, 0.54 ± 0.02*m*, 0.78 ± 0.01*m*, 1.13 ± 0.04*m*, 2.34 ± 0.05*m*, and 5.34 ± 0.07*m*.

To minimize experimental time, solutes were injected as mixtures three times per mixture into the gas chromatograph. The

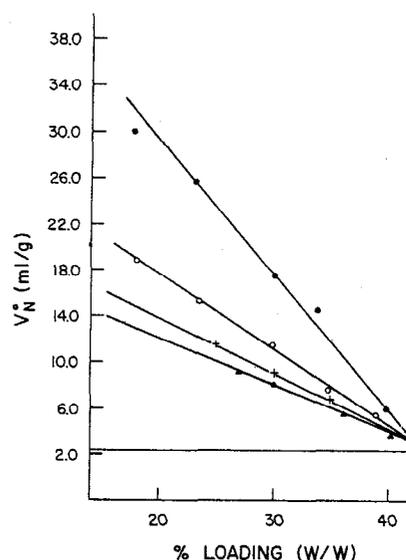


Figure 2. V_N^0 vs. % loading for fluorobenzene on the following stationary phases. (\blacktriangle) 0.54*m* NaCl, (+) 1.13*m* NaCl, (O) 2.34*m* NaCl, (\bullet) 5.34*m* NaCl, temp. = 12.5 °C, (—) no additive

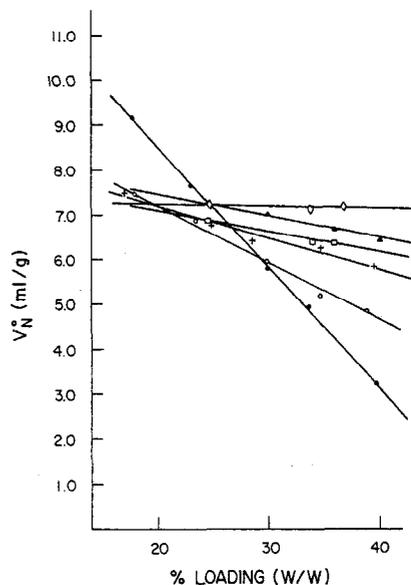


Figure 3. V_N^0 vs. % loading for dichloromethane on the following stationary phases. (\diamond) 0.25*m* NaCl, (\blacktriangle) 0.54*m* NaCl, (\square) 0.78*m* NaCl, (+) 1.13*m* NaCl, (O) 2.34*m* NaCl, (\bullet) 5.34*m* NaCl, temp. = 12.5 °C

head space of the vials containing the mixture were sampled with a 10.0 μ l gas-tight syringe and injected directly onto the column. By using this technique, one can obtain the small sample sizes required in this study.

RESULTS AND DISCUSSION

Figures 1, 2, and 3 present the change in V_N^0 for different types of solutes with stationary phase loading as a function of additive (salt) concentration. For *n*-nonane in Figure 1, there is a dramatic increase in V_N^0 as the % loading is decreased; an indication of the dominance of the adsorption term in Equation 1. Although this effect has been noted before (4), it is further amplified by the addition of electrolyte to the stationary phase. In fact, at a 20% loading, V_N^0 is increased 44-fold over that recorded for the retention of *n*-nonane on a pure water column (4)!

In Figure 2, the same data are plotted for fluorobenzene as a solute. As noted previously (4), the V_N^0 for fluoroben-

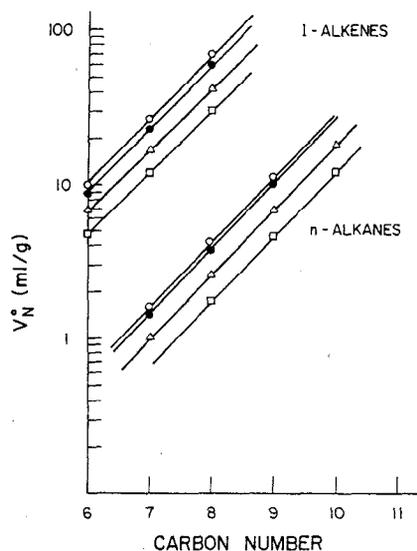


Figure 4. Logarithm of V_N^0 vs. carbon number for n -alkanes and 1-alkenes on various % loadings. Concentration of $\text{Ca}(\text{NO}_3)_2 = 5.4M$, Support = Chromasorb P, Temp. = 12.5°C . The values of V_N^0 for the 1-alkenes have been multiplied by a factor of 10. (O) 10% loading, (●) 15% loading, (Δ) 20% loading, (\square) 31% loading

zene is constant with change in the loading at zero additive concentration (pure water); an indication that both terms in Equation 1 are contributing to the net retention volume. This trend can be changed dramatically by the addition of electrolyte as illustrated in Figure 2. Here, the salting-out of the nonelectrolyte from the aqueous salt solution decreases the $K_L V_L^0$ term in Equation 1 and amplifies the $K_A A_L^0$ term as shown by the sharp rise in the slopes of the V_N^0 -% loading plots with increasing electrolyte concentration. An additional interesting feature of the data plotted in Figure 2 is that the V_N^0 -% loading functions extrapolate to the same point in the high % loading region; close to the mean of the V_N^0 values recorded for pure water as the stationary phase (4). Such a regular trend is in part due to the small, but finite $K_L V_L^0$ term for fluorobenzene which is always less in magnitude than the $K_A A_L^0$ term regardless of the electrolyte concentration employed.

The trend in V_N^0 with % loading for dichloromethane at various electrolyte concentrations is quite different from that exhibited by n -nonane and fluorobenzene. Dichloromethane exhibits considerably more solubility than either n -nonane or fluorobenzene at all salt concentrations (1); hence, the $K_L V_L^0$ term has a considerable leveling effect on the change in V_N^0 with % loading. This is amply illustrated in Figure 3. It is also important to note that this effect permits the same net retention volume to be obtained by varying not only the A_L^0/V_L^0 ratio, but by varying the electrolyte concentration too, as evidenced by the intersection of the V_N^0 -% loading plots as a function of electrolyte concentration.

To illustrate the selectivity trends possible using electrolyte additives to the stationary phase in GLC, Figure 4 presents the net retention volume/gram of packing for n -alkanes and 1-alkenes adsorbing on $5.4M$ $\text{Ca}(\text{NO}_3)_2$ aqueous solutions coated at various % loadings. The trends illustrated in Figure 4 are similar to those obtained on pure water columns (6), i.e., an increasing V_N^0 with decreasing stationary phase loading. Further examination of Figure 4 reveals that the relative retention between homologs of the same series, e.g., n -octane and n -nonane, and members of different homologous series having the same carbon number, e.g., n -octane and 1-octene, is constant. This has also

Table I. Relative Retention as a Function of % Loading^a

	% Loading/solute				
	18.04%	23.45%	29.86%	34.69%	38.86%
Benzene	1.00	1.00	1.00	1.00	1.00
Toluene	3.03	2.88	2.82	2.64	2.46
Ethylbenzene	7.22	6.90	6.71	6.09	5.51
Carbon tetrachloride	1.00	1.00	1.00	1.00	1.00
Chloroform	2.66	2.65	2.81	3.26	3.88
Dichloromethane	1.62	1.77	2.11	2.83	3.84

^a Temp: 12.5°C . Molality: $2.34m$ NaCl.

been found true for n -alkanes, 1-alkenes, branched alkanes, and alicyclic saturated hydrocarbons on aqueous NaCl columns (1).

The above results indicate that no selectivity advantage is gained by varying the % loading of the stationary phase at a constant electrolyte concentration for solutes which are retained by one sorption mechanism. However, this is not the case for solutes which weakly partition into the stationary phase. Table I tabulates the relative retention for several aromatic solutes and chlorinated hydrocarbons on $2.34m$ NaCl column as a function of stationary phase loading. These figures are relative to the V_N^0 of benzene and carbon tetrachloride, respectively. For the aromatic solutes, the greatest selectivity is exhibited at the low loadings of stationary phase where the relative difference in adsorption constants for the solutes at the gas-liquid interface are largest and this difference is amplified by the A_L^0 factor.

As the loadings are increased, the first term in the rhs of Equation 1 is minimized with respect to the overall retention for a particular solute; hence, the partition term may become significant depending on the relative values of K_L at a particular electrolyte concentration. Since the relative retention of ethylbenzene with respect to toluene is approximately constant (a factor of 2.34), this implies that the partition term for the benzene is contributing to the net retention volume. These trends are not surprising considering that toluene and ethylbenzene are all but effectively salted-out of the electrolyte solution at this particular salt concentration, however, benzene has a small, but finite K_L (1), which accounts for the recorded variation of relative retention for the benzene/toluene and benzene/ethylbenzene pairs.

For the chlorinated hydrocarbons, the retention patterns are much more complex. The relative retention of chloroform and dichloromethane with respect to carbon tetrachloride increases with liquid loading indicating the importance of the partition term. Although carbon tetrachloride weakly partitions into water, it is all but effectively retained by adsorption at the gas-liquid interface on the $2.34m$ NaCl column. It is interesting to note that on the 39% loading column, chloroform and dichloromethane are retained equally, indicating that the relative contributions of the $K_L V_L^0$ term to V_N^0 for each solute is off-set by the difference in their relative adsorption coefficients. This would seem to indicate that by changing the electrolyte concentration at this particular loading, chloroform and carbon tetrachloride could easily be separated.

Table II shows relative retention as a function of electrolyte concentration for several classes of solutes at 39% loading. In each case, the relative retention is defined relative to the net retention volume of 1-pentene, benzene, and carbon tetrachloride, respectively. The trends shown for the olefinic solutes are typical of solutes which do not undergo

Table II. Relative Retention as a Function of Electrolyte Concentration (NaCl)^a

	Electrolyte concentration/solute		
	1.13m ^b	2.34m ^c	5.34m ^d
1-Pentene	1.00	1.00	1.00
1-Hexene	2.23	2.47	2.51
1-Heptene	...	5.97	6.22
1-Octene	11.70	14.60	15.80
2-Octene	12.80	16.40	16.90
Benzene	1.00	1.00	1.00
Toluene	1.93	2.46	2.97
Ethylbenzene	3.76	5.51	7.36
Carbon tetrachloride	1.00	1.00	1.00
Chloroform	4.84	3.88	2.81
Dichloromethane	5.74	3.84	2.24

^a Temp: 12.5 °C. ^b 39.52% loading. ^c 38.86% loading. ^d 39.73% loading.

partition into the aqueous electrolyte solutions. Here, the net retention volumes increase with salt addition for each member of the homologous series; however, solutes of higher carbon number are selectively retained to a greater degree. This trend is also exhibited for the same homologous series on Ca(NO₃)₂ columns (6). Similar retention patterns are also displayed for alkylated aromatic solutes in Table II. Such a trend seems to confirm the hypothesis that the introduction of a hydrophobic moiety into the solute will increase the retention of that solute relative to its parent structure.

The retention trends for the chlorinated hydrocarbons as a function of electrolyte concentration are interesting. At 2.34m NaCl, as noted previously, the retention of these two solutes is approximately equal, while at the highest electrolyte concentration, dichloromethane elutes before chloroform. This is a direct result of their relative adsorption and partition coefficients, the K_A of chloroform being greater than that for dichloromethane over the entire range of NaCl concentrations examined while the reverse situation holds true with regard to the relative trends in K_L .

Earlier workers (7-11) have also shown the advantages gained by the addition of electrolyte to the stationary

phase on the separation of solutes in GLC. Unfortunately, these studies have attributed the bulk of the retention behavior and, hence, the selectivity exhibited, to the bulk retention mechanism term, $K_L V_L^\circ$. Where these workers have acknowledged the possibility of adsorption at the gas-liquid interface (8, 10), their experiments do not permit the ascertainment of its importance to the retention mechanism. If the data presented in this study are typical, then we feel that some of the assumptions of Wasik and coworkers (10, 11) and Bigli et al. (8, 9) are unwarranted.

CONCLUSIONS

The stationary phase systems discussed above show high and variable selectivity characteristics for different types of solutes. Whereas the thermal stability of the aqueous electrolyte stationary phases is limited, the principles illustrated in this study would not preclude the use of less volatile solvents (7). Further, the increase in V_N° of a solute with electrolyte addition to the stationary phase shows that the increase in K_A with additive concentration must be taken into account in studies of bulk distribution processes via chromatographic methods.

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