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ADSORPTION OF POLAR SOLUTES ON LIQUID-MODIFIED SUPPORTS

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SUMMARY

The experimental technique of mass spectrometric tracer pulse chromatography was used to measure the equilibrium isotherms of acetone with *n*-hexadecane coated on different chromatographic supports. A model is proposed and shown to be accurate for these systems at three temperatures. The model is based on the assumptions that: (i) total adsorption is simply the sum of the liquid and solid contributions; (ii) these mechanisms operate independently; and (iii) there is no measurable liquid surface adsorption at the temperatures and pressures used in this investigation.

INTRODUCTION

Liquid-modified and vapor-modified adsorbents constitute a significant class of chromatographic stationary phases. Liquid-modified adsorbents include any active support, such as the diatomaceous earth and graphitized carbon black supports, coated with a non-volatile stationary liquid phase. Vapor-modified adsorbents would be those encountered in the use of steam¹, formic acid^{2,3}, dodecane⁴, and other organic vapors^{5,6} as carrier gases in gas chromatography (GC). In the particular case of the graphitized carbon blacks, many studies have shown that small amounts of either vapors^{7,8} or liquids⁹ can have significant, and often unpredictable, effects upon the chromatographic properties of these common adsorbents.

The mechanism for the retention of infinite dilution solutes with these "modified" adsorbents is not well understood, and little quantitative work, in the form of equilibrium isotherm measurements, has been carried out because of the experimental difficulties involved in the study of these complex, multicomponent systems. Because of the paucity of quantitative data, there are controversial, and often contradictory, reports in the literature concerning the effect of sample size and liquid surface adsorption for systems involving polar solutes and non-polar liquid phases.

The effect of these modifiers at low surface coverages is to neutralize very active adsorption sites on the adsorbent surface and, in general, to diminish the retention of any solute due to competitive adsorption. Commonly, however, the effect of increased amounts of modifier is enhanced retention of some solutes due to cooperative adsorption effects on the solid⁹, liquid surface adsorption¹⁰, or normal bulk liquid solubility effects. The effect of the solid support adsorption should be independent of

the amount of modifier at surface coverages of a monolayer or more^{11,12}. Solid support effects appear to diminish as the amount of modifier or liquid phase is increased because of the greater contribution from solution effects; however, the effect of the modified solid is often not negligible even at high liquid loadings.

Enhanced retention of solutes, with a maximum at some intermediate surface coverage or liquid loading, has been observed in diverse systems and attributed to equally diverse causes. Such behavior has been observed for acetone in squalane and attributed to solid support adsorption¹³, for 2-butanone in octadecane and attributed to liquid surface adsorption¹⁰, for benzene in polybutylene¹⁴ and squalane¹⁵ and not attributed to any cause. One of the few studies in which equilibrium isotherms were determined¹² does not really clarify the problem because the conclusion in that study was that the amount of squalane coated on Chromosorb P had little or no influence on the amount of acetone adsorbed up to 7–10% coating and that adsorption in this system was mainly solid support adsorption which was not influenced by the amount of modifier (squalane) present.

It is possible that these reports are not as contradictory as it appears. Conder¹⁶ has proposed that the neglected parameter in these comparisons is the pressure of the solute in the gas phase or the mole fraction of the solute in the liquid phase. The suggestion is that liquid surface adsorption of polar solutes will only be observed at very low pressures and mole fractions of less than 0.02, even though Liao and Martire¹⁷ observed liquid surface adsorption for "solution dominated" (large sample size) elution samples. Serpinet¹⁸ has also suggested that the contradictory results concerning the existence of liquid surface adsorption for these systems is due to pooling of non-polar liquids on the surface of silanized supports which diminishes the liquid surface area. On the other hand, Mathiasson and Jönsson¹⁰ observed significant liquid surface adsorption of ketones on octadecane coated on dimethylchlorosilane (DMCS) treated supports.

In this investigation, we have used a new experimental technique¹⁹, called mass spectrometric tracer pulse chromatography (MSTP), to measure the equilibrium isotherms of a polar solute in a non-polar solvent coated on active and deactivated supports in an attempt to elucidate the adsorption mechanism in these complex systems.

EXPERIMENTAL

The experimental procedure, instrumentation, coating and analysis procedures were the same as described previously^{8,19}.

The isotope effect on the solubility of d_6 -acetone in hexadecane was determined from the relative retention times of deuterio- and natural acetone at three temperatures. The ratio of the solubility of acetone to that of the heavy isotope at 30, 45, and 60°C were 1.03, 1.01, and 0.98 respectively. This data was used to correct all of the isotherm data for isotope effects.

The liquid phase was *n*-hexadecane (Alltech) and the solid supports were Chromosorb P AW (Applied Science Labs.) and Chromosorb P AW DMCS (Johns-Manville). The supports were 60–80 mesh and the columns were made from 1/4 in. O.D. copper tubing in lengths from 100 to 300 cm. The percent loadings varied from 5 to 32%.

The isotopic solute was d_6 -acetone (99.8%) (Commissariat Pour L'Energie Atomique, France). The gaseous mixtures used for the carrier gas were composed of the isotopic acetone in helium with mole fractions of acetone up to 0.06. The mole fractions were determined on a separate gas chromatograph with a thermal conductivity detector by comparison with the peak areas of samples of helium saturated with acetone at several temperatures lower than ambient.

RESULTS

The systems chosen for investigation were acetone with *n*-hexadecane coated on different common chromatographic supports. Acetone is a typical "polar" solute and the necessary heavy isotope is readily available as a common NMR solvent. The solvent and supports are common chromatographic systems that have been studied extensively for solid support and liquid surface adsorption. These systems with a polar solute and non-polar solvent were chosen for study because they represent a significant class of systems for which it is often difficult, if not impossible, to abstract thermodynamic solubility and adsorption data from chromatographic results because of the multiple retention mechanisms which may prevail in these systems.

The difficulties encountered with these systems are illustrated in Fig. 1 which is a plot of the specific retention volume of acetone for various sample sizes on active and deactivated supports. The plots are somewhat similar to those observed by Mathiasson and Jönsson¹⁰ and are indicative of complex retention mechanisms, including non-ideal solution effects. The variation of the specific retention volume with sample size in these systems is significant, even for the DMCS treated support. Especially at

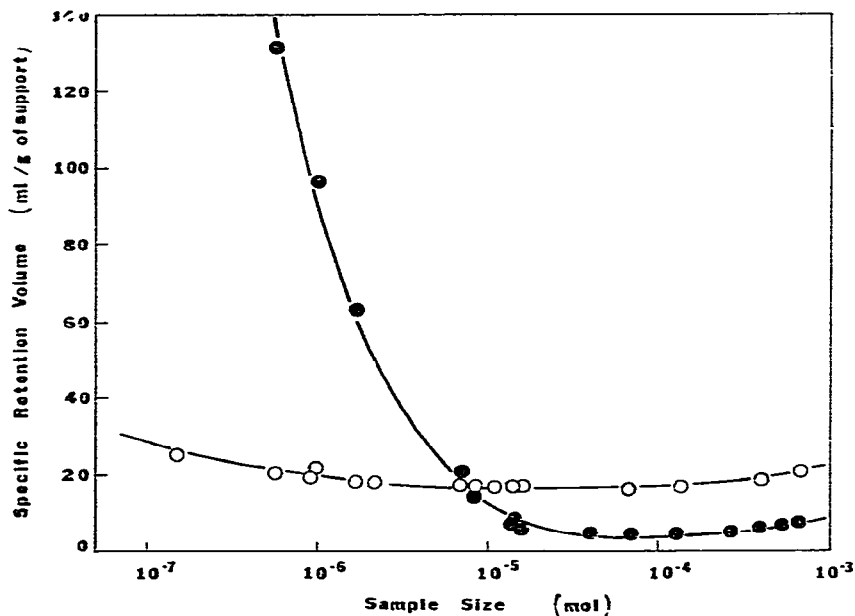


Fig. 1. Specific retention volume of acetone in *n*-hexadecane. ●, Chromosorb P AW; ○, Chromosorb P AW DMCS.

low pressures, the variation is dramatic, and there is no indication that the linear region of the adsorption isotherm, *i.e.*, infinite dilution conditions, can be attained with any practical sample size for the untreated support. However, there have been a great number of schemes suggested for abstracting the solubility data for acetone in hexadecane from this type of data. These procedures all involve the measurement of a retention parameter over a range of either sample size^{10,17} or liquid loading^{17,20} with an extrapolation (usually non-linear) to zero sample size and/or infinite liquid loading. These procedures have been critically reviewed and compared by several authors^{10,17,20}.

In an attempt to develop a model for these systems, adsorption isotherms were measured at a series of temperatures for acetone in *n*-hexadecane coated on both active and deactivated supports. The data for the deactivated (DMCS treated) supports is given in Table I and shown in Fig. 2. The variation of the activity coefficient with mole fraction was not always linear; however, the variation with pressure was linear in each case and the limiting activity coefficients obtained from a linear regression are given in Table II and compared with static literature data in Fig. 3. The agreement with literature data is good. This data was obtained from two different columns with 20 and 30% liquid coating on deactivated support, and there is no evidence of liquid surface adsorption in these systems. The DMCS support is not completely inert and the uncoated support does adsorb about 25% as much acetone

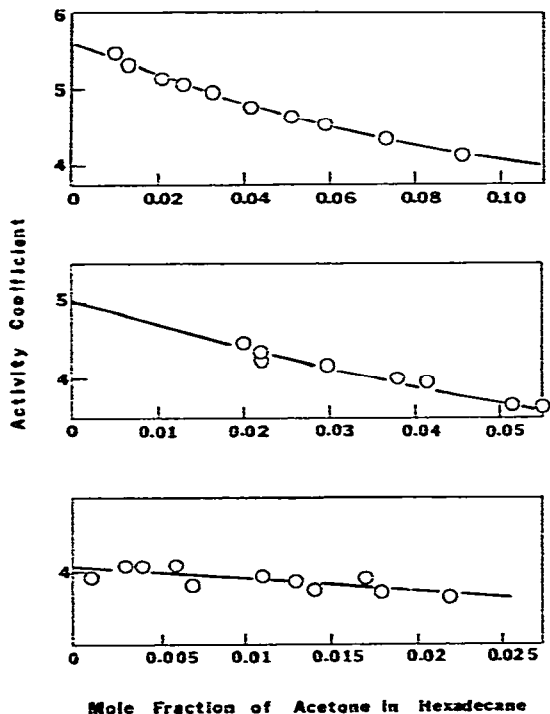


Fig. 2. Activity coefficient of acetone in *n*-hexadecane as a function of liquid phase composition. Top, 30°C; middle, 45°C; bottom, 60°C.

TABLE I
SOLUBILITY DATA FOR ACETONE IN *n*-HEXADECANE COATED ON CHROMOSORB P AW DMCS

30°C		45°C		60°C	
Liquid mole fraction	Activity coefficient	Liquid mole fraction	Activity coefficient	Liquid mole fraction	Activity coefficient
0.010	5.44	0.020	4.46	0.001	3.92
0.013	5.30	0.024	4.23	0.003	4.10
0.021	5.12	0.024	4.35	0.003	4.07
0.026	5.07	0.030	4.18	0.004	4.08
0.033	4.96	0.030	4.16	0.006	4.10
0.042	4.75	0.038	4.00	0.007	3.81
0.051	4.62	0.043	3.95	0.011	3.93
0.059	4.52	0.053	3.64	0.013	3.87
0.073	4.34	0.055	3.62	0.014	3.73
0.091	4.11			0.017	3.91
				0.018	3.71
				0.022	3.68

as the uncoated AW support; however, the large amounts of liquid coating used in this study effectively swamped out any residual adsorption on the DMCS supports.

Adsorption isotherms of this same system on an active support (Chromosorb P AW) were also determined under the same conditions. These results are given for 30°C in Table III and Fig. 4 as the open data points. The specific retention volume data is given per gram of solid support so there is an increase in the retention volume with liquid loading, however, the shape of the isotherm is indicative of surface adsorption, as well as, bulk liquid solubility.

In previous studies similar to this one, Urone and co-workers^{11,12} proposed a model for solid support effects in which adsorption by a covered (modified) surface was shown to be independent of the liquid loading as long as the surface was covered

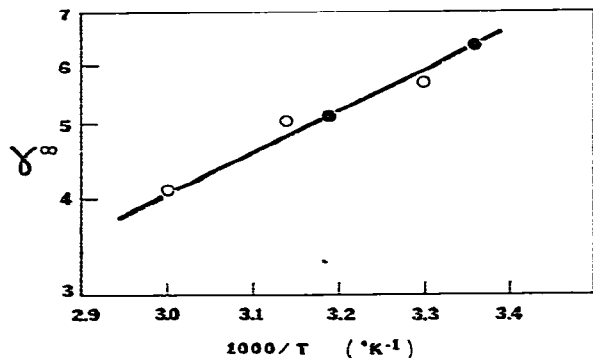


Fig. 3. Infinite dilution activity coefficients of acetone in *n*-hexadecane at various temperatures. O, This work; ●, literature²¹.

TABLE II
INFINITE DILUTION ACTIVITY COEFFICIENTS OF ACETONE IN *n*-HEXADECANE

	Temperature (°C)	Limiting activity coefficient
This work	30	5.6
	45	5.0
	60	4.1
Literature ²¹	25	6.3
	40	5.1

by more than a monolayer of liquid. This model was tested for the present systems by subtracting out the calculated liquid solubility contribution from the overall adsorption given in Table III. The liquid contribution was calculated from the pressure dependence of the activity coefficients given in Table I. The closed data points in Fig. 4 show the results of this correction for each liquid loading. The three corrected isotherms are identical, within experimental error, and independent of both liquid loading and liquid surface area (which is higher for the lowest percent coating). The solid line through this corrected data is for a Langmuir isotherm with $k_1 = 1.0$ and $k_2 = 0.07$. The adsorption isotherm of acetone on uncoated Chromosorb P AW is also shown in Fig. 4. This data is in agreement with the "corrected" isotherms showing, again, that *n*-hexadecane has little or no influence on the adsorptive properties of the solid support.

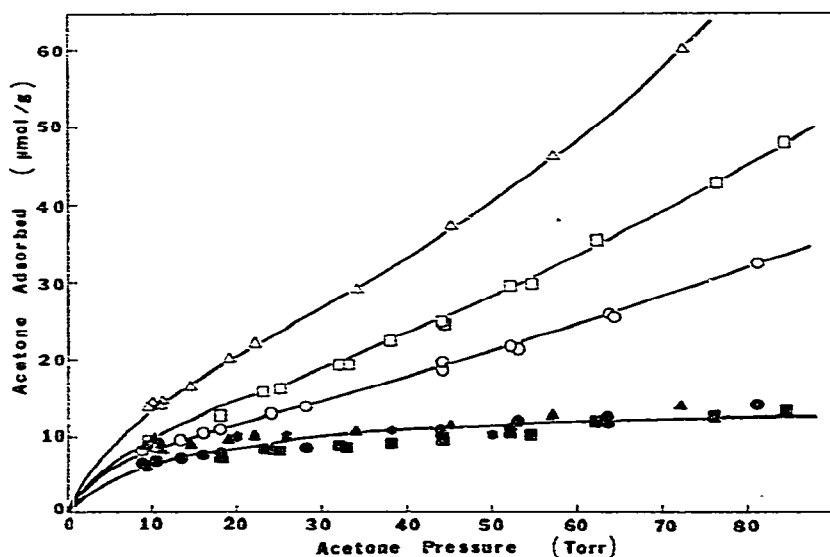


Fig. 4. Equilibrium isotherms of acetone in *n*-hexadecane on Chromosorb P AW at 30°C. Coating: ▲, △ 15%; ■, □ 10%; ●, ○ 5%; ★, 0%.

TABLE III

SORPTION ISOTHERMS FOR ACETONE AT 30°C IN *n*-HEXADECANE ON CHROMOSORB P AW

5% Coating		10% Coating		15% Coating	
Pressure (Torr)	Acetone adsorbed ($\mu\text{mol/g}$)	Pressure (Torr)	Acetone adsorbed ($\mu\text{mol/g}$)	Pressure (Torr)	Acetone adsorbed ($\mu\text{mol/g}$)
9.1	8.0	9.6	9.6	9.5	13.7
10.2	8.5	18.0	12.5	10.7	14.0
13.6	9.5	23.1	15.8	10.7	14.5
18.0	10.9	25.1	16.2	11.6	14.7
23.9	12.7	31.8	19.3	13.9	16.5
28.2	13.8	32.7	19.5	19.4	20.0
43.8	19.5	38.2	22.3	22.3	21.9
44.4	18.7	43.7	24.8	33.8	29.2
51.7	21.5	43.9	24.8	44.7	32.1
53.3	21.3	51.7	29.5	56.8	46.6
63.3	25.8	53.8	29.7	72.2	60.0
63.9	25.4	61.9	35.3		
81.0	32.6	75.8	42.6		
		84.1	48.0		

Similar experiments were carried out for two liquid loadings at 45 and 60°C and the results are shown in Figs. 5 and 6. The corrected isotherms for the solid supports are independent of liquid loading in each case, and there is little temperature dependence for adsorption on the liquid-modified solid surface.

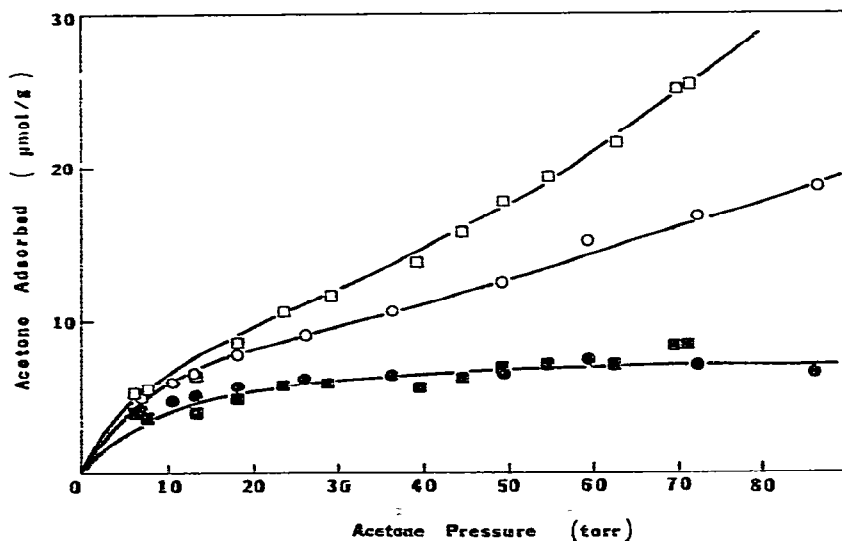


Fig. 5. Equilibrium isotherms of acetone in *n*-hexadecane on Chromosorb P AW at 45°C. Symbols as Fig. 4.

TABLE IV
RESULTS OF NON-LINEAR REGRESSION OF DATA ON CHROMOSORB P AW

Regression sets (percent coatings)	γ'			k_1			k_2		
	30°C	45°C	60°C	30°C	45°C	60°C	30°C	45°C	60°C
5 and 10%	7.3	4.9	3.8	1.0	-0.017	-0.011	1.2	0.20	0.16
5 and 15%	5.4			1.5	-0.033	-0.015		0.07	
10 and 15%								0.12	
5, 10, and 15%									
Data from DMCS-treated supports	5.6	5.0	4.1	1.5	-0.018	-0.013	0.7	0.10	0.06
					-0.020	-0.006	0.8	0.07	

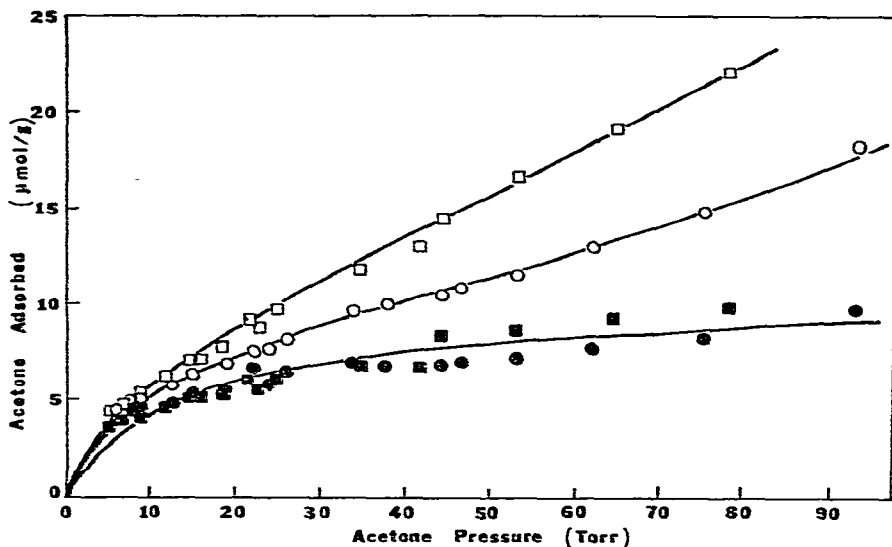


Fig. 6. Equilibrium isotherms of acetone in *n*-hexadecane on Chromosorb P AW at 60°C. Symbols as Fig. 4.

DISCUSSION

If the activity coefficient is a linear function of pressure and the modified solid adsorption follows a Langmuir isotherm, the total adsorption isotherm can be described by

$$n_T = \frac{n_{1p}P}{\gamma^\infty P^0 + (\gamma'P^0 - 1)P} + \frac{k_1P}{1 + k_2P} \tag{1}$$

where n_T and n_{1p} are the amount of solute and solvent in the stationary phase per gram of solid ($\mu\text{mol/g}$), P^0 is the vapor pressure of pure acetone, γ^∞ and γ' are the infinite dilution activity coefficient and the first derivative of the activity coefficient with respect to the pressure, P , and k_1 and k_2 are the constants in the Langmuir isotherm equation. This model assumes that there is no liquid surface adsorption, that the solid surface adsorption is controlled solely by the mole fraction of acetone in the liquid, and that solution and adsorption effects are mutually independent.

If this adsorption model is correct, the four adjustable parameters, γ^∞ , γ' , k_1 and k_2 in eqn. 1 should be attainable from a mathematical regression of the data for the total sorption isotherms on the active supports at two or more liquid loadings. These parameters were determined for the data in Table II with a general non-linear least squares computer program and the results are given in Table IV, along with the results obtained from the solvent on the deactivated support and the "corrected" solid adsorption isotherms.

These mathematical results indicate that accurate solubility and adsorption data can be obtained chromatographically for liquids coated on active supports and that the model used to derive eqn. 1 is an accurate description of these systems. There

is no evidence of liquid surface adsorption of acetone on hexadecane at the temperatures and pressures used in this investigation. This does not preclude the existence of liquid surface adsorption of polar solutes on non-polar liquids at lower pressures, however, it is more probable that solid support adsorption would dominate at lower pressure even with DMCS treated supports.

The pressure range covered in this study is larger than the pressure range normally encountered in elution GC. It was necessary to attain higher pressures in order to observe the liquid solubility contribution relative to the solid support adsorption. Urone *et al.*¹² found that the amount of acetone adsorbed by squalane coated Chromosorb P AW at a fixed pressure was independent of the amount of squalane present because the pressure used was only about 14 Torr. At this low pressure there is little liquid contribution and the solid support adsorption is not significantly affected by the amount of liquid coating as shown in Figs. 4-6. These systems with high liquid loads at low pressures are very similar to systems with low liquid loads at higher pressures. In both cases, the predominant retention mechanism is adsorption on the liquid-modified adsorbent, and the liquid coating has little or no influence on the total adsorption in either case.

Even though it is possible to evaluate the separate adsorption and solution mechanisms by frontal chromatography, as in this study, a more significant objective would be to do the same thing directly from elution experiments. The retention volume is proportional to the derivative of n_T with respect to P at each pressure, *i.e.*, the slope of the isotherm. Differentiation of eqn. 1 gives a direct relation between the specific retention volume of an elution peak and the mean pressure of the solute. The missing factor is an accurate relation between this pressure and the sample size of the elution sample. The "effective" pressure of an elution sample will likely be a complex function of several variables, such as sample size, retention volume, height equivalent to a theoretical plate (HETP), temperature, flow-rate, and liquid loading.

CONCLUSIONS

Chromatographic supports covered with more than a monolayer of a non-polar liquid or vapor will adsorb polar solutes to an extent that is determined solely by the mole fraction of the solute in the liquid and independent of the amount of liquid or vapor "modifier". The total adsorption is simply the sum of solid and liquid contributions, as first pointed out by Urone and co-workers^{11,12}. The amount of solute adsorbed on the solid surface is a function of temperature and pressure, and can be adequately described by a Langmuir isotherm equation.

The simple model, represented by eqn. 1, is adequate to allow the accurate determination of activity coefficients and the composition dependence of these activity coefficients of a polar solute in a non-polar solvent coated on an untreated chromatographic support. The experiments must be carried out at relatively high pressures using frontal rather than elution techniques at present. However, this model can, hopefully, be used to develop a simple technique for correcting normal elution data for the effects of solid support adsorption.

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