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Determination of the Activity Coefficient of a Volatile Component in a Binary System by Gas-Liquid Chromatography

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The gas-liquid chromatographic (GLC) method of measuring the activity coefficient of the solute in a binary system has been extended from infinite dilution to the finite concentration range. An equation is presented relating the retention volume of the injected solute sample to the equilibrium solute concentration present in the column. This relation permits determination of the activity coefficient of the solute. Based on the experimental results obtained from the study of the two binary systems, benzene in diethylene glycol at 50°, 70°, and 90°C. and *n*-hexane in 1,2,4-trichlorobenzene at 30°C., the activity coefficients of the solute measured by the GLC method were found to agree within about ±5% with those obtained by the static equilibrium method.

The vapor-liquid equilibrium of a volatile solute in a relatively nonvolatile solvent is difficult to measure by the conventional static equilibrium method because of the low equilibrium concentration of the solvent in the vapor phase and similarly the low concentration of the solute in the liquid phase. A number of investigators (*1, 4, 5, 9, 11, 13, 17*) have measured the activity coefficient of a solute at infinite dilution in such a nonvolatile solvent by the gas-liquid chromatographic (GLC) method. In this method the time required for a small solute sample to be carried through the column by an insoluble carrier gas, such as helium, is measured. The vapor-liquid equilibrium constant K and hence the activity coefficient may be calculated from the retention volume by the equation

$$V_N = \overline{V}_G + \frac{1}{K}\left(\frac{\rho_L}{\rho_G}\right)\overline{V}_L \qquad (1)$$

The derivation of Equation (1) by Martin and Synge (*12*) and others (*9, 10, 15*) is based on the plate model and includes the assumptions that the sample size injected is small and no solute vapor is present in the insoluble carrier gas prior to the injection of the solute. The activity coefficient measured by this method is the activity coefficient of the solute at infinite dilution.

The object of the present study was to extend the GLC method for measuring the activity coefficient of the solute in a binary system from infinite dilution through a measurable concentration range. To accomplish this, a gaseous mixture of solute vapor and helium gas, instead of pure helium (or other inert gas), was used as the carrier gas. After the column had been flushed by the gaseous mixture for a sufficient length of time, the nonvolatile solvent inside the column became saturated with the solute, and hence an equilibrium state between the vapor phase and liquid phase was reached. Both phases contained a finite amount of solute. A small sample of the solute was then injected into the carrier gas entering the column, and its retention time was measured. The activity coefficient was calculated from the apparent retention time from the theoretical model presented below. By varying the concentration of the solute in the carrier gas, activity coefficients at various concentrations of the binary solution were determined. The experimental results have been compared with activity coefficient measurements obtained by others from vapor-liquid equilibrium measurements.

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THEORETICAL BACKGROUND

A mathematical analysis of the process of injecting into a chromatographic column a sample composed of a molecular species already present in the elution gas has been studied by Stalkup and Deans (*19*). An analytical solution for a binary elution gas was obtained by them based on a mathematical model which included the assumptions of point equilibrium and negligible longitudinal diffusion. A simplified expression applicable for the dilute concentration range has been given by Helfferich and Peterson (*6*). Both of these papers pointed out that because the retention time is a function of dy/dx rather than y/x, in order to obtain the equilibrium constant from retention time, experiments should be performed by increasing the concentration of y in small increments. From such data the curves of K vs. y may then be generated through an iteration procedure. Stalkup and Kobayashi (*20*) have measured K values of propane in a number of methane-propane elution mixtures containing propane up to 25.55 mole %. However, for that particular system dy/dx happened to be not significantly different from K; thus a simplified equation instead of the above mentioned iteration procedure was employed by them to calculate K. No other experimental measurements of K values in the finite concentration by the GLC method have been reported.

An equation which expresses the retention volume obtained on injecting a small solute sample into a chromatographic column through which a gaseous mixture of the solute vapor and in insoluble carrier gas have been flowing continuously may be derived based on the same ideal stage (or theoretical plate) model which has been adopted by various authors (*9, 10, 12, 15*) to derive Equation (1). Because the volume of a mixture is, generally, a complex function of concentration, to simplify the material balance the general equation given below has been derived on a molal basis instead of the conventional volumetric basis.

Starting with the material balances around stage p, one obtains

$$dN_{p-1} - dN_p = dG_p + dL_p \tag{2}$$

$$y_{p-1}dN_{p-1} - y_p dN_p = d(G_p y_p) + d(L_p x_p) \tag{3}$$

$$L_p = \frac{m_s}{1 - x_p} \tag{4}$$

Following a mathematical treatment similar to that used by Keulemens (*9*) to derive Equation (1), one obtains the following equation:

$$N_m = \overline{G} + \frac{\overline{m}_s(1-y)}{(1-x)^2}\left(\frac{dx}{dy}\right) \tag{5}$$

Conversion of Equation (5) from mole units to more conventional volume units gives

$$V_N = \overline{V}_G + \overline{V}_L\left(\frac{1-y}{1-x}\right)\frac{\rho_L}{\rho_G}\left(\frac{dx}{dy}\right) \tag{6}$$

One may also derive Equation (6) from Equation (16) presented by Stalkup and Dean (*19*). The major advantage of the ideal stage approach described above is that no assumption of point equilibrium is required.

When one compares Equation (6) with Equation (1), it is easy to see that Equation (6) reduces to Equation (1) when y and x are infinitesimally small, and thus the term dx/dy may be approximated by the reciprocal of K, the vapor-liquid equilibrium constant at infinite dilution. When one compares Equation (6) with Equation (5) given by Helfferich and Peterson (*6*), it can also be seen that the latter equation is valid only when x and y are small or nearly equal, that is, when the term $(1-y)/(1-x)$ is approximately unity.

Since at equilibrium

$$x = \frac{y}{K} \tag{7}$$

$$\frac{dx}{dy} = \frac{1}{K}\left[1 - \frac{y}{K}\left(\frac{dK}{dy}\right)\right] \tag{8}$$

Equation (5) may be rearranged to obtain

$$K = \frac{1}{2}(2y + ab) + \frac{1}{2}[(2y + ab)^2 - 4y^2]^{1/2} \tag{9}$$

where

$$a = \frac{(1-y)\overline{m}_s}{(N_m - \overline{G})f_p} \tag{10}$$

$$b = 1 - \frac{y}{K}\left(\frac{dK}{dy}\right) \tag{11}$$

$$f_p = \left(\frac{3}{2}\right)\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \tag{12}$$

The quantity f_p is a correction term given by James and Martin (*7*) to account for the effect of the change of the density of the gas phase caused by the small pressure drop across the column.

Because of the b term, Equation (9) cannot be solved analytically other than when $y = 0$. However, it can be solved numerically through an iterative procedure if $(N_m - \overline{G})$ is measured at various values of y, starting at $y = 0$ and then increasing y by small increments. Through Equations (9), (10), (11), and (12), a curve of K vs. y may then be generated.

The activity coefficient of the solute in the liquid phase is defined as

$$\gamma_{2L} = \frac{K P_m}{P_2^o}\Phi \tag{13}$$

where Φ is defined as

$$\Phi = \frac{f_{2v} P_2^o}{y P_m f^o_{2L}} \tag{14}$$

Equations (9) and (13) relate γ_{2L} to $(N_m - \overline{G})$. From Equation (5) and (8), it can be seen that $\overline{G}$ is merely the N_m of a solute sample, such as air, with K approaching infinity. $(N_m - \overline{G})$ thus can be obtained by simply measuring θ_R, the time interval between the appearance of the concentration peaks of the air and solute samples which are injected simultaneously, and then multiplying it by N_f, the molal flow rate of the gaseous mobile phase:

$$N_m - \overline{G} = N_f\theta_R \tag{15}$$

It should be emphasized that Equation (5) is derived on the assumption that the size of solute sample injected is infinitesimally small. Only under such conditions will the instantaneous concentrations in each stage after the injection x_p and y_p be essentially the same as the concentrations x and y before injection. In practice, however, a finite amount of solute sample (generally between 0.1 to 1.0 μliter) is required to produce a visible chromatographic peak. To obtain the true value of $(N_m - \overline{G})$, several measurements at various sample sizes should be made and the value of $(N_m - \overline{G})$ obtained by extrapolation to zero sample volume.

EXPERIMENTAL

Systems and Materials

The binary systems, diethylene glycol—benzene and 1, 2, 4-trichlorobenzene—*n*-hexane, were selected for the present study for the following reasons:

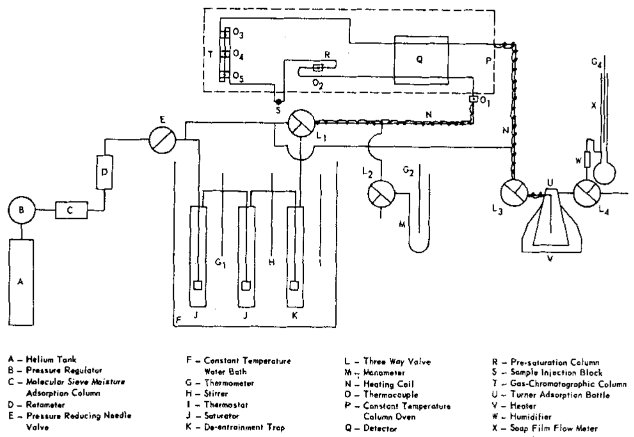

Fig. 1. Schematic diagram of equipment.

1. Relatively low vapor pressure of diethylene glycol and 1, 2, 4-trichlorobenzene: 1.2 mm. Hg at 90°C. and 0.82 mm. Hg at 30°C., respectively.
2. Suitable volatility of benzene and *n*-hexane; 200 mm. Hg at 42.2° and 31.6°C., respectively.
3. Phase equilibrium data of the two binary systems, obtained from static equilibrium measurements by Pierotti et al. (*16*) and Neckel and Kohler (*17*), were available for comparison.

The diethylene glycol used had a boiling point specification of 128° to 130°C. at 10 mm. Hg. Its refractive indexes, measured in this laboratory, were $N_D^{25°C.} = 1.44535$ and $N_D^{20°C.} = 1.44710$, respectively. The latter value agrees well with $N_D^{20°C.} = 1.4472$ reported by Curme and Johnston (*3*). Analysis was made with a Perkin-Elmer Vapor Fractometer with a Q column at a temperature of 220°C. No impurities could be found.

Benzene was recrystallized twice in this laboratory. The solid portion, which had a refractive index $N_D^{25°C.} = 1.49792$, the same value reported by the API Project 44 (*18*), was retained. Analysis by the Fractometer with a diethylene glycol column indicated that the purified benzene contained less than 0.02 wt. % of impurities.

The 1, 2, 4-trichlorobenzene used had a melting point specification of 17°C. Analysis by the Fractometer with a Q column at 175°C. indicated it contained five different trace impurities, amounting to an estimated total of 1.5 wt. %. After three recrystallizations, the impurities were reduced to 0.5 wt. %. The melting point of the purified product was determined at 16.8° to 16.9°C. which agrees well with the values given in the International Critical Tables (16.6°C.) (*22*) and by Neckel and Kohler (16.7°C.) (*14*).

The *n*-hexane used was pure grade with a specification of 99% minimum purity. Analysis with an A column indicated that it contained less than 0.5 wt. % impurities. Its refractive index $N_D^{20°C.} = 1.37491$ corresponded closely to the value $N_D^{20°C.} = 1.37486$ reported by API Project 44 (*18*).

The experimental GLC columns used were prepared particles of Johns-Manville Firebrick C-22 as the inert solid support material. After carefully screening, the sieved 14- to 20-mesh size particles were washed with distilled water and then dried in an oven at 300°C. for 3 hr. before being coated with diethylene glycol or 1, 2, 4-trichlorobenzene. The coatings were applied under a reduced pressure of 30 mm. Hg to prevent the absorption of atmospheric moisture by the coating liquids, especially the diethylene glycol.

Apparatus and Procedure

The schematic diagram in Figure 1 gives the general layout of the experimental apparatus. The carrier gas, containing a definite amount of solute vapor (benzene or *n*-hexane), was prepared by passing the helium gas stream through saturators (*J*) containing liquid benzene or *n*-hexane. The solute-saturated helium which left the de-entrainment trap (*K*) was led by copper tubing into the chromatographic column (*T*) inside the column oven of a modified Fractometer. The temperature of the wall of the copper tubing was maintained at a temperature above the temperature of the water bath (*F*) by an electrically heated coil (*N*) and fiber glass insulation to prevent the condensation of solute vapor in the carrier gas stream. The gas chromatographic column (*T*) was packed with firebrick particles coated with the absorbing solvent (diethylene glycol or 1, 2, 4-trichlorobenzene). The temperature of the oven surrounding the column was maintained within ± 0.1°C. After the solute-saturated carrier gas had been passed through the chromatographic column (*T*) for at least half an hour, a stable base line on the recorder of the vapor fractometer indicated that an equilibrium condition had been reached inside the column, because the base line could be maintained at a constant level only when the concentration of solute in the column inlet stream was the same as that in the exit stream.

The equilibrium concentration of solute in the helium gas stream was determined by adsorption of the solute on activated charcoal. After the state of equilibrium had been reached inside the chromatographic column, the Turner (*21*) adsorption bottle (*U*), filled with activated charcoal, was connected to the exit end of the column. The period of adsorption was carefully timed. The flow rate of solute-free helium from the exit end of the Turner adsorption bottle was measured by a soap-film flow meter (*X*).

Samples of liquid solute in the range of 0.1 to 10 μliters were injected into the chromatographic column (*T*) through the sample injection block (*S*), where a small heater vaporized the sample immediately. The liquid samples were injected along with 1.0 to 5.0 μliters of air. Thus an air peak and a solute peak both appeared on the recorder chart. The time interval between the appearances of the two peaks was the apparent retention time θ_R. Various sizes of samples were injected in random order to study the effect of sample size on the retention time. The smallest sample size used in each run in general was below 1.0 μliter.

After four to ten samples had been injected during an adsorption time of over 40 min., the Turner adsorption bottle (*U*) was closed off and disconnected from the gas stream. The difference in the weight of the adsorption bottle before and after the adsorption, corrected for the amount of solute injected, was the net amount of solute adsorbed from the carrier gas stream. The mole fraction of solute in the gaseous mobile phase y thus can be calculated by the following equation:

$$\frac{y}{1\text{-}y} = \frac{W_2 M_2}{N_f' \theta_D} \tag{16}$$

TABLE 1. EXPERIMENTALLY MEASURED VALUES OF *a* [EQUATION (10)]*

Benzene—Diethylene glycol						*n*-Hexane—1,2,4-trichlorobenzene	
50°C.		70°C.		90°C.		30°C.	
y	*a*	*y*	*a*	*y*	*a*	*y*	*a*
0.0	2.435	0.0	4.67	0.0	8.46	0.0	0.696
0.0	2.410	0.0	4.61	0.0	8.40	0.0	0.696
0.0	2.400	0.0	4.68	0.1678	7.25	0.0288	0.527
0.0	2.380	0.0507	4.47	0.2970	6.61	0.0340	0.506
0.0	2.382	0.0644	4.33	0.3164	6.62	0.0483	0.431
0.0433	2.179	0.0812	4.26	0.3350	6.42	0.0610	0.366
0.0489	2.066	0.0899	4.19	0.3438	6.39	0.0799	0.293
0.0627	1.972	0.1038	4.03	0.4050	5.94	0.0928	0.229
0.0632	2.016	0.1226	3.78	0.4460	5.88	0.1066	0.1183
0.0791	1.912	0.1464	3.75	0.4615	5.62	0.1340	0.1197
0.0779	1.867	0.1900	3.53	0.5410	5.29		
0.0947	1.746	0.2104	3.35	0.5556	5.03		
0.1024	1.672	0.2334	3.24				
0.1153	1.668	0.2472	3.27				
0.1237	1.590	0.2741	3.05				
0.1242	1.586	0.3089	2.761				
0.1437	1.422	0.3430	2.625				
0.1449	1.432	0.4406	1.980				
0.1801	1.229	0.5235	1.443				
0.2184	0.978	0.5556	1.346				
0.2410	0.859						
0.2788	0.619						
0.3004	0.457						

* Column pressure of 745 mm. Hg.

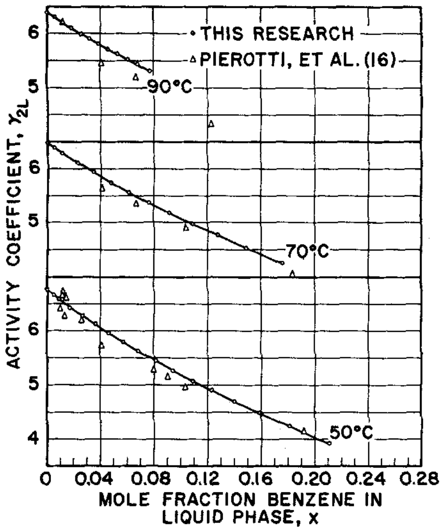

Fig. 2. Activity coefficients of benzene in diethylene glycol.

The mole fraction calculated by Equation (16) was compared with that computed from the vapor pressure of solute at the temperature of the saturators, based on the assumption that the saturation was completed. The deviation, in general, was less than 3%. Further information on both apparatus and procedures is available (*2*).

EXPERIMENTAL RESULTS AND DISCUSSION

Activity coefficients of benzene in the binary system of diethylene glycol and benzene were determined at three different temperature levels, covering the concentration ranges of benzene in liquid phase from zero to 21.1 mole % at 50°C., zero to 17.6 mole % at 70°C., and zero to 7.74 mole % at 90°C., respectively. In accordance with the experimental data of Johnson and Francis (*8*), diethylene glycol and benzene are completely miscible in this diethylene glycol-rich range, although they form two partially miscible phases at higher concentrations of benzene.

The activity coefficients of *n*-hexane in the second binary system of 1,2,4-trichlorobenzene and *n*-hexane were measured only at 30°C. The concentration of *n*-hexane in the liquid phase covered a range from zero to 31.9 mole %.

It was noticed that the measured quantity $(N_m - \overline{G})$ was slightly dependent upon the size of solute sample injected. During each run, in general, four to ten samples of various sizes from 0.1 up to 10 μliters were injected. The measured value of $(N_m - \overline{G})$ was plotted against the volume of sample injected. The extrapolated value of $(N_m - \overline{G})$ at zero sample volume was substituted into Equation (10) to obtain the quantity a. The reciprocal of a has the equivalent physical meaning of specific retention volume in a conventional chromatographic column. The experimentally measured a for the two binary systems at different temperatures are listed in Table 1.

From the values of a listed in Table 1, curves of a vs. y were plotted. Based on the value of a read from these smoothed curves at equal intervals of y, K was then calculated from Equations (9) and (11) by the following procedure: K at infinite dilution was directly read from the a vs. y curve because at $y = 0$, $b = 1$, $K = a$. A trial value of K was then assumed at $y = 0.01$, and the term b was calculated from Equation (11) by setting dK/dy equal to $\Delta K/\Delta y$ between $y = 0$ and $y = 0.01$. A value of a for $y = 0.01$ was read from the a vs. y curve. The K calculated from Equation (9) were compared with the initially assumed K. Adjustments were made until agreement between the assumed and calculated K was finally achieved. K at other values of y were calculated by the same procedure.

Activity coefficients were calculated from the final values for K by Equation (13). The correction factor (Φ) for the imperfection of the vapor phase, was calculated from the following equation:

$$\ln \Phi = \ln \frac{Z^{\circ}_2}{Z_m} - 2(Z^{\circ}_2 - 1) - \frac{V_{2L}}{RT}(P_m - P^{\circ}_2) + \frac{2P_m}{Z_m RT}(y_1 B_{12} + y_2 B_{22}) \tag{17}$$

The correction factor Φ varied from 0.993 to 1.044.

The derivation of Equation (17) and the selection of second virial coefficients of the two binary systems studied have been discussed elsewhere (*2*).

The mole fraction of solute in the liquid phase was obtained by substituting y and K into Equation (7).

The activity coefficients determined by the GLC method are plotted against the mole per cent of solute in the liquid phase in Figures 2 and 3 in order to compare them with the activity coefficients calculated from vapor-liquid equilibrium data measured by Pierotti et al. (*16*) and Neckel and Kohler (*14*). The activity coefficients computed from these static equilibrium data were corrected for gas imperfection from Equation (17). Smoothed values of activity coefficients given by Neckel and Kohler (*14*), corrected for gas imperfection by using a somewhat different correction procedure, differ only slightly from those computed from Equation (17) and shown in Figure 3.

For these two binary systems at 50° and 30°C., respectively, the agreement between the data obtained by the GLC method and those obtained by the static equilibrium method appear to be within the overall experimental error of both methods. For the system of diethylene glycol-benzene at 70° and 90°C., the activity coefficients obtained by the GLC method are slightly higher than the corresponding values obtained by Pierotti et al. However, except for a few points, the activity coefficients obtained from the two methods agree to within ± 5%.

CONCLUSIONS

The GLC method of measuring the activity coefficient of the solute in a binary system has been extended from infinite dilution to the finite concentration range. Based on the experimental results obtained from the study of the two binary systems: diethylene glycol–benzene at 50°, 70°, and 90°C. and 1,2,4-trichlorobenzene–*n*-hexane at 30°C., the activity coefficients measured by the GLC method are found to agree to within approximately ±

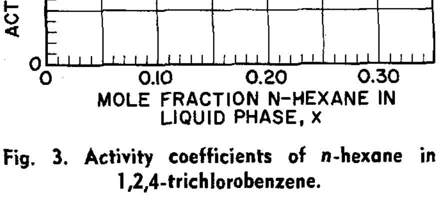

Fig. 3. Activity coefficients of *n*-hexane in 1,2,4-trichlorobenzene.

5% with those obtained by other investigators using the static equilibrium method.

ACKNOWLEDGMENT

The authors are deeply indebted to Messrs. F. I. Stalkup and Friedrich Helfferich for their contributions to the theoretical analysis of this problem, especially for pointing out to us that $dK/dy \neq 0$, as had been assumed by us in an earlier treatment (2).

NOTATION

B_{22}, B_{12} = second virial coefficient of component 2 and the interaction coefficient for the mixture of component 1 and 2, respectively

f_p = pressure correction factor as defined by Equation (12)

f^{o}_{2L} = fugacity of pure solute in the liquid phase at T and P_m

f_{2V} = fugacity of solute in the vapor phase

G_p = number of moles of gas in stage p

$\overline{G}$ = total number of moles of gaseous phase inside a gas chromatographic column

K = vapor-liquid equilibrium constant of solute, y/x

L_p = number of moles of liquid including the absorbed solute in stage p

$\overline{L}$ = total number of moles of liquid phase including the absorbed solute inside a gas chromatographic column

M_2 = molecular weight of solute

m_s = number of moles of absorbing solvent in each stage

$\overline{m}_s$ = total number of moles of absorbing solvent inside a chromatographic column

N_f = molal flow rate of the gaseous mobile phase

N_f' = molal flow rate of solute-free helium stream

N_m = number of moles of the gaseous mobile phase which has passed through a gas chromatographic column when the concentration of the solute at the end of the column is maximum

N_p = number of moles of the gaseous mobile phase which has passed through stage p

P_i = pressure at the inlet of a gas chromatographic column

P_o = pressure at the outlet of a gas chromatographic column

P_m = mean pressure inside a gas chromatographic column, $(P_i + P_o)/2$

P^{o}_2 = vapor pressure of solute

p = ordinal number of ideal stage

R = gas constant

T = absolute temperature inside a gas chromatographic column

V_N = retention volume

$\overline{V}_G$ = total volume of gas (vapor) phase inside a gas chromatographic column

$\overline{V}_L$ = total volume of liquid phase including the absorbed solute inside a gas chromatographic column

V_{2L} = molal volume of solute in the liquid state at T

W_2 = weight of solute adsorbed by the activated charcoal

x = mole fraction of solute in the liquid phase of a chromatographic column prior to the injection of the solute sample

x_p = mole fraction of solute in the liquid phase in stage p

y = mole fraction of solute present in the gaseous mobile phase of a chromatographic column prior to the injection of the solute sample

y_p = mole fraction of solute in the gaseous mobile phase in stage p

y_1 = mole fraction of carrier gas (component 1) in the vapor phase

y_2 = mole fraction of solute vapor (component 2) in the vapor phase

Z_m = compressibility factor of gaseous mixture at T and P_m

Z^{o}_2 = compressibility factor of solute vapor at T and P_2^{o}

Greek Letters

ρ_G = moles per unit volume of gas inside a column at T and P_o

ρ_L = moles per unit volume of liquid including the absorbed liquid inside a column at T

Φ = correction factor for the imperfection of vapor phase as defined by Equation (14)

γ_{2L} = activity coefficient of solute in the liquid phase as defined by Equation (13)

θ_R = apparent retention time

θ_D = length of the time during which the solute in the column exit was adsorbed by the activated charcoal

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