# Thermodynamics of Solution by Gas Chromatography of Some Heterocyclic Compounds

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**Solute activity coefficients at infinite dilution in some heterocyclic compounds like furfuryl alcohol, furfuryl amine, and tetrahydrofurfuryl alcohol used as stationary phases in gas-liquid chromatography have been measured for 33 nonelectrolytic binary systems (11 solutes and three solvents). Data are presented for elution at 27°C. Activity coefficients of benzene and hexane in tetrahydrofurfuryl alcohol systems are compared with previous published data for the same binary systems. Some characteristics of solute-solvent interactions in the systems are discussed.**

The gas chromatographic (gc) technique has been well established as an effective and advantageous method for determining thermodynamic properties at infinite dilution for binary nonelectrolyte solutions. The chromatographic data so obtained were in good agreement with those obtained from static equilibrium measurements (*4*). Almost all cited work involved determination of physical constants for volatile solutes in so-called nonvolatile stationary phases, the deterrent factor for using the volatile phases being, perhaps, the nonstationary nature of these solvents. But some workers (*5, 12, 14*) have sought to alleviate this problem of bleeding out of the phase by using suitable forecolumns or presaturators to saturate the carrier gas with solvent at the system's temperature and pressure upstream of the gas chromatographic column. The use of volatile solvents as stationary phase in gas chromatography, notwithstanding the experimental difficulties, merits detailed studies as information derived from such data can be successfully utilized in separation problems, especially in petroleum fields, or conversely, these data could augment other studies for physical chemists. The present study seeks to extend this gc technique to include systems with heterocyclic volatile solvents which were used as stationary phases. This extension permits the measurement of thermodynamic equilibrium parameters of more common binary solutions often needed by chemical engineers and physical chemists.

The furan nucleus is less reactive than other compounds such as cyclopentadiene with a similar system of double bonds as the *p*-orbitals of the oxygen atom and the $\pi$-orbital of the diene systems overlap forming an aromatic system somewhat similar to that in benzene but with much lower resonance energy (*3, 11*) and the conjugation is less efficient than in benzene as explained lucidly by Badger (*1*). Because of the interesting electronic structure it was considered worthwhile to look into these three five-membered heterocyclic aromatic compounds having different substituents attached to the furan rings, namely furfuryl alcohol (FA), furfuryl amine (FAm), and tetrahydrofurfuryl alcohol (THFA) for the study of thermodynamics of solution of some selected hydrocarbons by gc. In an earlier communication (*7*) from this laboratory, the use of FAm as gc stationary phase was reported where it was indicated that this solvent had the potentiality for the rapid analysis of lighter hydrocarbons, a fact also substantiated by the same type of studies (*8*) carried out on FA and THFA phases.

The activity coefficient for solute at infinite dilution in a stationary phase $\gamma^\infty$ may be related to the gc measured specific retention volume $V_g{}^0$ by the equation (*4, 9, 10*)

$$\gamma^\infty = \frac{1.704 \times 10^7}{MP^0\, V_g{}^0} \tag{1}$$

where $M$ is the molecular weight of the stationary liquid phase (solvent), $P^0$ refers to the vapor pressure of the pure solute vapor in mm of mercury abs and $V_g{}^0$ is the specific corrected retention volume of the solute in ml of carrier gas per gram of liquid. Giddings and Mallik (*4*) and Martire and Pollara (*9*) have discussed the assumptions, explicit and implicit, underlying the derivation of Equation 1. We have pointed out (*4*) that the data in these cases are no more precise than is the location of the center of eluted peaks, and one would have to take into account errors due to the noncompensating errors stemming from detector and recorder time lag and from extra-column dead volume. Fortunately such difficulties do not lead to errors larger than ±1%. Another assumption in this technique has been that the vapor phase above solution and the pure solute vapor both behave ideally, and the pure solute is chosen as the standard state—i.e., $\gamma^\infty \rightarrow 1$ as $x \rightarrow 1$ where $x$ is the solute mole fraction. The specific retention volume, $V_g{}^0$ was determined from the well-known expression developed by Littlewood and co-workers (*6*) given by the equation

$$V_g{}^0 = \frac{F_m t_R}{W} \times \frac{273.2}{T_f} \times \frac{P_o - P_w}{P_o} \times \frac{3(P_i/P_o)^2 - 1}{2(P_i/P_o)^3 - 1} \tag{2}$$

where

$F_m$ = carrier gas flow rate measured with soap-film meter at column outlet, ml/min
$t_R$ = time between the air and solute peak maxima, min
$W$ = weight of stationary liquid, grams
$T_f$ = temperature of soap-film meter, °K
$P_i$ = column inlet pressure, mm of Hg abs
$P_o$ = column outlet pressure, mm of Hg abs
$P_w$ = vapor pressure of water, mm of Hg abs at $T_f$

## EXPERIMENTAL

The chemicals (FA, THFA, and FAm) were obtained from Fluka (Switzerland) and Koch-Light Lab., England, and were distilled prior to use. The three solvents were used as typical gc stationary phases and impregnated on the solid support in the conventional manner. Approximately 28% coating on Chromosorb P (50–60 mesh size) was used for all our studies, the columns were always prepared under identical conditions using 2-m (3-mm diam) copper tubing. The data were taken at 27 ± 0.2°C using hydrogen as the carrier gas in a Chrome Alyser gas chromatograph equipped with a thermal conductivity detector. The pressure difference across the column was measured with a mercury manometer, and the gas flow was monitored by a calibrated soap-film (flow rate) meter at the outlet. To eliminate the problem of solvent depletion, precolumns (about 30 cm length of 3 mm diam) packed with about 35% of the desired solvent-coated support material was used so that the carrier gas was saturated with solvent prior to the point of sample injection. Satisfactory functioning of the presaturator column was reflected in the stability of the base line as no dis-

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cernible changes were observed throughout the brief experimental work.

The first step in preparation for an experiment was the accurate determination of the weight of coated supports in the column. The packed column was placed in the chromatograph, and the carrier gas hydrogen was passed through the presaturator and the column. Before the saturated gas stream entered the system's solute injection part, its pressure was measured with a mercury manometer. This pressure was taken as the inlet pressure of the chromatographic column. The outlet pressure was at all times atmospheric. The column's gas volume was determined from each experiment by injecting 25 $\mu$l of air. Samples ranging from 0.5–1 $\mu$l of liquid solutes and in case of gas samples, 20 $\mu$l of solutes were injected on-column using 10- or 100-$\mu$l Hamilton syringes, respectively. The retention time for each solute was measured from the air peak to sample peak maxima. (Vapor pressures were evaluated from the Antoine equation constants, API Project No. 44.) Reproducibility of the present study's activity coefficients presented in Table I varied from ±2% for *n*-hexane to ±10% for *n*-pentane in furfuryl amine and from ±3% for benzene to ±6% for *n*-hexane in furfuryl alcohol. In case of tetrahydrofurfuryl alcohol, reproducibility of the data was better as compared with the other two solvents and varied mostly between ±2–6%.

## RESULTS AND DISCUSSIONS

In the three stationary phases it was possible to resolve mixtures of saturated and unsaturated hydrocarbons in a very short time. The chromatograms of all these compounds showed symmetric peaks useful for analytical purposes (*8*). The actual process of determining the thermodynamic properties from gc consists of measuring the chromatographic parameters experimentally (*4*) and then employing Equations 1 and 2 to compute the desired results. Table I gives the activity coefficients of 11 solutes in the solvents. The data represent average values for three runs on each binary system. The table clearly indicates that all the compounds studied exhibit a marked positive deviation from Raoult's law.

The activity coefficients decrease numerically as the polarity of the solvent decreases from FA to THFA. The data obtained in FAm solvent in the majority of cases lie somewhere between FA and THFA values. The activity coefficient is related to the excess partial molar free energy $g^{-E^\infty}$ by the well-known equation $g^{-E^\infty} = RT \ln \gamma^\infty$. As $g^{-E^\infty}$ is exponentially related to the activity coefficient, the trends observed in Table I are somewhat normalized in Figure 1, showing an incremental relationship between excess free energy and molecular structure for hydrocarbon solutes in the three solvents at 27°C.

The validity of any data under the equilibrium condition can be substantiated by comparison with existing results in the literature, but no direct data for comparison are available for these solvents. However, Deal and Derr (*2*) had reported the limiting activity coefficients for two solutes, hexane and benzene, in tetrahydrofurfuryl alcohol. Their data at 25°C are given as 15 and 2.2, which are in close agreement with our data of 14.7 and 2.2 at 27°C for hexane and benzene, respectively; the selectivity factor $\gamma_H^\infty/\gamma_B^\infty$ for the said solutes in THFA is 6.8 which compares favorably with our value of 6.7.

**Table I. Infinitely Dilute Activity Coefficients for Hydrocarbons in Furfuryl Alcohol, Tetrahydrofurfuryl Alcohol, and Furfuryl Amine at 27°C**

| Solutes | Furfuryl alcohol | Furfuryl amine | Tetrahydro-furfuryl alcohol |
|---|---|---|---|
| Ethane | 11.4 | 6.5 | 6.1 |
| Propane | 14.1 | 9.5 | 8.0 |
| *n*-Butane | 18.3 | 10.8 | 9.7 |
| *i*-Butane | 19.9 | 11.7 | 10.4 |
| *n*-Pentane | 24.0 | 11.5 | 12.0 |
| *n*-Hexane | 31.1 | 13.8 | 14.7 |
| *n*-Heptane | 41.9 | 16.0 | 17.6 |
| Cyclohexane | 18.0 | 9.1 | 8.7 |
| Methylcyclopentane | 18.0 | 9.0 | 9.2 |
| Cyclohexene | 9.6 | 5.5 | 5.4 |
| Benzene | 3.8 | 2.3 | 2.2 |

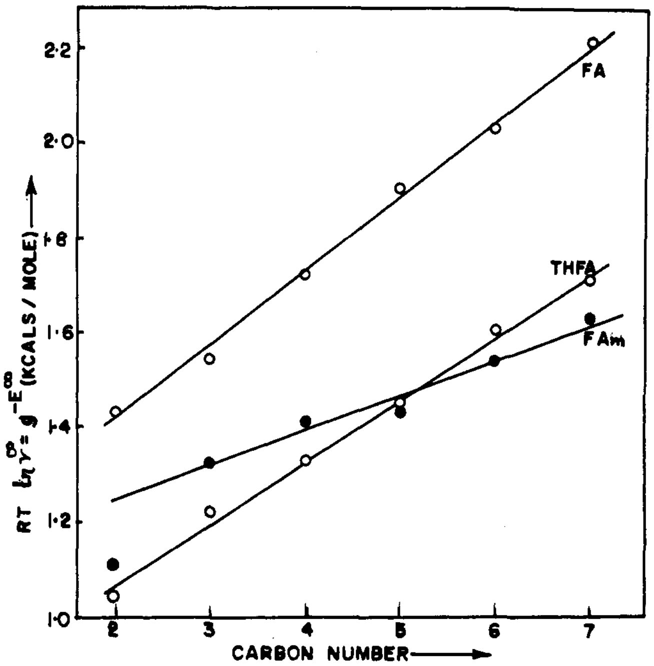

Figure 1. Incremental relationship between excess free energy and molecular structure for hydrocarbon solutes in furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), furfuryl amine (FAm)

## NOMENCLATURE

$\gamma^\infty$ = activity coefficient for solute at infinite dilution
$M$ = molecular weight of the stationary phase
$P^0$ = vapor pressure of the pure solute vapor, mm of Hg abs
$V_g^0$ = specific corrected retention volume of the solute, in ml of carrier gas per gram of liquid
$F_m$ = carrier gas flow rate, ml per min

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RECEIVED for review December 21, 1970. Accepted October 12, 1971.