$$T = x_1 T_1^0 + x_2 T_2^0 + x_3 T_3^0 + \omega + \sum_{i,j=1}^{3} x_i x_j \sum_{k=0}^{l} C_K(x_i - x_j)^k$$
$$+ x_1 x_2 x_3 [A + B(x_1 - x_2) + C(x_1 - x_3)$$
$$+ D(x_2 - x_3) + \ldots] \quad (12)$$

where l is the number of terms in the series expansion of $(x_i - x_j)$ and

$$\omega = x_1 \ln (y_1/x_1) + x_2 \ln (y_2/x_2) + x_3 \ln (y_3/x_3) \quad (13)$$

Again, the contribution of ω can be neglected. The different constants of eq 12 appear in Table II and, from the value of the root mean square deviation, the correlation is good. The ternary isothermals were calculated with eq 12 and are presented in Figure 1.

Acknowledgment

Yehudit Reizner and Kohav Ben-Zaken helped in the experimental and numerical determinations.

Glossary

α, β A, B, C	constants
B_i	second virial coefficient, cm^3/mol
B_{ij}	mixed virial coefficient, cm^3/mol
n	number of experimental points
N	number of components
P	total pressure, mmHg
P_i^0	vapor pressure of component i pure, mmHg
R	gas constant, cal/(g mol K)
rmsd	root-mean-square deviation, $[\Sigma_i^n \Sigma_j^n (y_{ji,exptl} - y_{ji,calcd})^2/3n]^{1/2}$
t, T	temperature, C, K
T_i^0	boiling temperature of component i at pressure P, K
V_i^0	molar liquid volume of component i pure, cm^3/mol
x_j, y_i	mole fraction composition of component i in the liquid and vapor phases

Literature Cited

(1) Boublikova, L., Lu, B. C. Y., J. Appl. Chem., 19, 89 (1969).
(2) Brandt, H., Rock, H., Chem.-Ing.-Tech., 29, 397 (1957).
(3) Bromiley, E. C., Quiggle, D., Ind. Eng. Chem., 25, 1136 (1933).
(4) Bushmakin, I. N., Kuznetsova, N. P., Zh. Prikl. Khim., 32, 1751 (1959).
(5) Hipkin, H., Myers, H. S., Ind. Eng. Chem., 46, 2524 (1954).
(6) Holzhauer, J. K., Ziegler, W. T., J. Phys. Chem., 79, 590 (1975).
(7) Katayama, T., Sung, E. K., Lightfoot, E. N., AIChE J., 11, 924 (1965).
(8) McDermott, C., Ellis, S. R. M., Chem. Eng. Sci., 20, 293 (1965).
(9) Quiggle, D., Fenske, M. R., J. Am. Chem. Soc., 59, 1829 (1937).
(10) Redlich, O., Kister, A., T., Ind. Eng. Chem., 40, 345 (1948).
(11) Rose, A., Williams, E. T., Ind. Eng. Chem., 47, 1528 (1955).
(12) Schneider, G., Z. Phys. Chem., 27, 171 (1961).
(13) Steinhauser, H. H., White, R. R., Ind. Eng. Chem., 41, 2912 (1949).
(14) TRC Tables, "Selected Values of Properties of Chemical Compounds", Thermodynamics Research Center Data Project, College Station, Texas, 1961.
(15) Tsonopoulos, C., AIChE J., 20, 263 (1974).
(16) Tsonopoulos, C., AIChE J., 21, 827 (1975).
(17) Vilcu, R., Cenuze, Z., Rev. Roum. Chim., 17, 367 (1972).
(18) Weber, J. H., Ind. Eng. Chem., 47, 454 (1955).
(19) Wisniak, J., Tamir, A., Chem. Eng. Sci., 31, 631 (1976).
(20) Wisniak, J., Tamir, A., J. Chem. Eng. Data, 20, 168 (1975).
(21) Wisniak, J., Tamir, A., J. Chem. Eng. Data, 22, 253 (1977).

Vapor–Liquid Equilibrium Data of Ethanethiol and Tetrahydrothiophene in Propane

John W. Goetzinger, Dennis W. Brinkman,* Bruce E. Poling, and Marvin L. Whisman

Bartlesville Energy Research Center, Energy Research and Development Administration, Bartlesville, Oklahoma 74003

Equilibrium K values for the odorants ethanethiol, tetrahydrothiophene, and a mixture of the two in propane were determined at −23, 0, and 35 °C. A technique was used in which samples from both the vapor and liquid phases were analyzed by gas chromatography, which gave K values to ±5%.

As part of a study to determine desired odorant concentrations in propane, the equilibrium odorant concentration in the vapor phase was measured for known concentrations in the liquid phase. This ratio of vapor concentration to liquid concentration, known as a K value (2), is important in obtaining proper odorant levels, yet the ratio has not been well established owing to adsorption problems and the low concentrations involved. When propane gas is released from a pressurized container, such as a consumer supply tank, the odorant-propane composition of the gas differs markedly from the composition in the liquid phase. This ratio of component concentrations is thus an important consideration in dosing the liquefied propane with the proper level of odorant for safe usage by the public. The value is also useful in fuel processing, since some mercaptans occur naturally and can cause problems by freezing out during production (9).

K values for various hydrocarbon mixtures have been published previously, and representative work is presented in ref 2, 6, and 9. These often have involved one alkane dissolved in another. More complicated systems, such as the sulfur-containing compounds used for odorization of natural gas and propane, have been studied only recently by Hankinson and Wilson (2). They found analysis by a gas chromatographic (GC) procedure to be unsatisfactory owing to adsorption of the sulfur compounds. Consequently, they based their studies on an end-point determination by olefactory detection—when one detected an odor, a titration endpoint had been reached. It was felt that a satisfactory GC procedure could be developed, as used with methanethiol (9), and this report describes the successful development of such a procedure. In addition, this study looks for possible interactions when a mixture of odorants is present. Such interactions would be important if the consumer uses more than one brand of liquid propane and does not completely empty the tank before refilling.

Although it has been shown that the K value does not change with liquid concentration over a fairly wide range (2), it does change with temperature. Three temperatures, −23, 0, and 35 °C (−10, 32, and 95 °F), representative of conditions found at various stages of storage and distribution of LP-gas, were selected. K values for ethanethiol (ethyl mercaptan), tetrahydro-
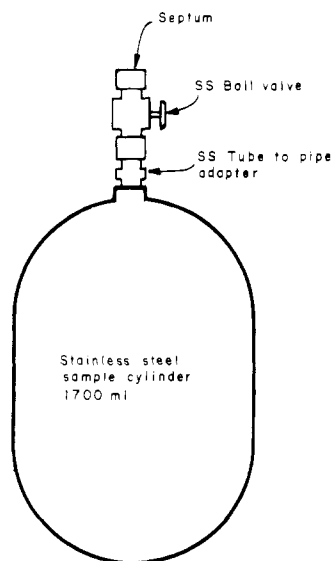
Figure 1. Blending cylinder and sampling system for determination of vapor–liquid equilibrium data.

Figure labels:
- Septum
- SS Ball valve
- SS Tube to pipe adapter
- Stainless steel sample cylinder 1700 ml

thiophene (thiacyclopentane or thiophane), and a mixture of the two in propane were obtained and compared with calculated (3, 4) values obtained previously by others.

Experimental Section

Sample Preparation. The blends of odorant and propane were prepared in stainless steel cylinders having an internal volume of 1.7 L. These containers were fitted, as shown in Figure 1, with a stainless steel ball valve and a septum for vapor sample extraction. The cylinder was evacuated, weighed to the nearest 0.1 g, charged with liquid propane, and then reweighed to determine the quantity of propane which had been charged. The average charge was 200 g. The volume of commercial grade ethanethiol and/or tetrahydrothiophene required to produce the desired concentration was then injected through the septum and ball valve with a microliter syringe. Concentrations used were about 20 ppm (mole/mole) ethanethiol and/or 200 ppm (mole/mole) tetrahydrothiophene. These gave vapor concentrations easily measured with gas chromatographic equipment (low ppm). Temperature equilibrium was attained by submerging the cylinders in a constant-temperature bath until analyses of the vapor taken several hours apart gave similar results. Equilibrium was speeded by attaching the cylinders to a Tekmar Model RM 18 stirring motor and rotating them in the baths at about 40 rpm.

Analytical Procedures. The concentrations of ethanethiol and tetrahydrothiophene were determined with a Perkin-Elmer 900 gas chromatograph, modified by the addition of a gas injection system that was operated at room temperature and consisted of a stainless steel gas-sampling valve fitted with a 5-mL sample loop constructed of 0.32-cm ($\frac{1}{8}$-in.) o.d. Teflon (FEP) tubing.

The helium carrier gas swept the sample into a packed column at a flow rate of 80 mL/min. The column was a 45-cm section of 0.32-cm o.d. Teflon (FEP) tubing packed with Supelco's "Supelpak-S". This is a specially prepared Porapak QS originally described by deSouza, Lane, and Bhatia (1). Temperature programming was used to obtain reasonable resolution between ethanethiol and propane while not overly prolonging elution of the less-volatile tetrahydrothiophene. The column temperature was held at 100 °C for 1 min, after sample injection, and then increased at a rate of 24 °C/min to a final temperature of 145 °C for ethanethiol or 190 °C for tetrahydrothiophene and the mixture and was held at that final temperature for 4 min. Under these conditions, retention times were about 0.2 min for propane, 2 min for ethanethiol, and 5 min for tetrahydrothiophene. The detector was a Perkin-Elmer flame photometric

detector held at 200 °C and fitted with a 394-nm narrow-band transmission filter. The resulting signals were recorded on a strip chart recorder equipped with an integrator. Peak areas were used to obtain odorant concentrations in both liquid and vapor phases, from which the observed K values were calculated.

Calibration. The chromatograph was calibrated with known concentrations of ethanethiol and tetrahydrothiophene in propane, prepared in Tedlar (polyvinyl fluoride) plastic bags, which were found to be excellent for preserving the integrity of calibration blends. A 1000-ppm sample was prepared in a bag fitted with a septum for injection of liquid odorant with a microsyringe. All standards were direct dilutions of aliquots of this stock sample. No standard, including the stock sample, was retained for more than 48 h.

Calibration samples were transferred from the Tedlar bag to the gas injection port of the chromatograph with a glass syringe. A calibration curve was drawn by use of peak areas given by the integrator. Each point on the curve represented an average of four–six samples with a maximum variation approximating ±4%. Concentration was proportional (approximately) to the square root of the area, so this represented a variation in concentration of ±2%. The lower limit of detection was less than 1 ppm for both ethanethiol and tetrahydrothiophene.

Sampling Procedure. Two sample procedures were used. Vapor samples were withdrawn from the colder test cells with a glass syringe fitted with a Teflon stopcock and a 5-cm, 23-gauge hypodermic needle. The ball valve on the sample cylinders was always open to promote equilibrium with all vapor, including that in the valving assembly, since this is the area from which the sample was extracted. Care was taken during the attachment and detachment of the stirring motor to make sure liquid sample was not splashed into the neck or above the open valve. For the −23 and 0 °C samples, the needle was inserted its entire length through the septum, and the Teflon stopcock on the syringe was opened to admit 15–20 mL of vapor sample into the syringe. However, the pressure was too high with the 35 °C samples, causing severe condensation of odorant as the gas rapidly expanded through the valves and needle. Therefore, samples at the highest temperature were collected by attaching an evacuated Tedlar bag via a Teflon valve. After connection, the valve on the bag was opened, followed by a quick opening and closing of the cylinder valve. This produced near 1 L of gas, which was about 5% of the total vapor above the liquid. Individual samples were then extracted from the bag as with the standards.

The liquid phase was sampled by inverting the test cylinder, removing the septum, and connecting the ball valve to an evacuated Tedlar bag. The valve on the bag and the ball valve on the cylinder were opened very briefly, allowing a small quantity of the liquid propane/odorant mixture to flow into the Tedlar bag. Since all of the liquid in the bag vaporized, almost immediately, the concentration of odorant in the resulting vapor was the same as it had been in the liquid. A portion of the resulting vapor was transferred to the chromatograph with a glass syringe in the same manner as with the standard mixtures. The K values of the odorant were determined by dividing the vapor concentration by the liquid concentration. These concentrations were determined from the calibration curves.

Four to six sample replicates were taken for analysis in all cases. The average of this series was then compared to the previous sample series in an attempt to determine whether the system had reached equilibrium. Thus, the final value was actually an average of at least eight replicates. The chromatographic system was checked before each series by injecting several aliquots of a standard ethanethiol–tetrahydrothiophene mixture containing 5 ppm of each odorant in propane.

Results and Discussion

The problems, mentioned by previous investigators, of poor reproducibility and condensations of odorant on metal parts were

Table I. K-Values for Ethanethiol, Tetrahydrothiophene, and a Mixture of the Two in Propane

					Odorant–propane system					
						Mixture				
	Temp		Ethanethiol Concn,[a]		Ethanethiol Concn,[b]		Tetrahydrothiophene Concn,[a]		Tetrahydrothiophene Concn,[a]	
°C	°F	°K⁻¹	K	ppm	K[b]	ppm	K[b]	ppm	K	ppm
−23	−10	0.0040	0.11	23	0.13	9.0	0.0089	160	0.007	193
0	32	0.00366	0.18	15	0.17	10.5	0.016	173	0.029	218
35	95	0.00325	0.22	32	0.26	10	0.036	179	0.033	215

[a] Concentration of odorant in the liquid phase (mole/mole). [b] Determined in mixture as if other odorant was not present.
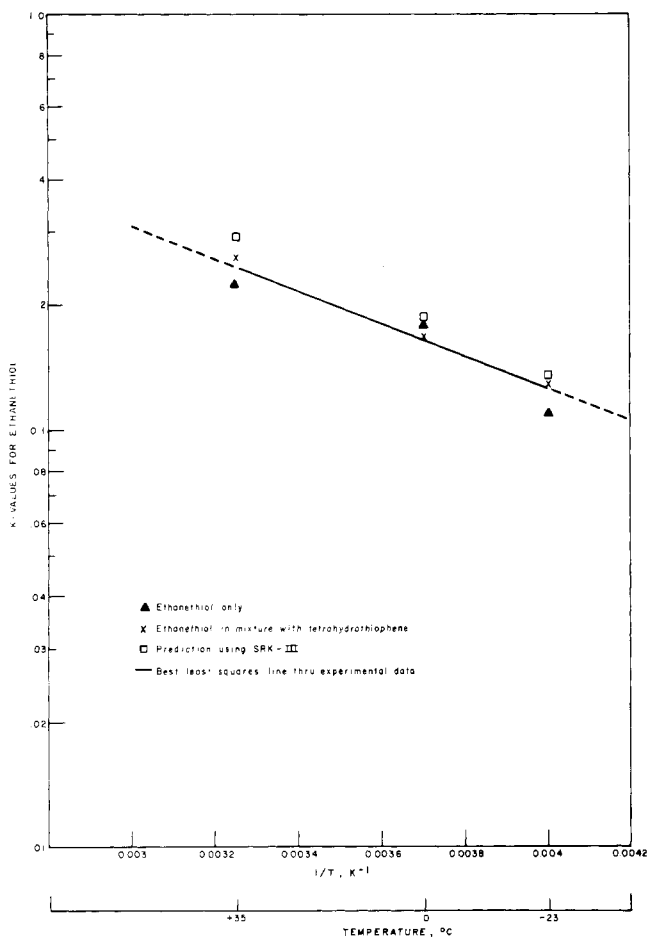

Figure 2. Theoretical and experimental K values for ethanethiol in propane as a function of the inverse of absolute temperature.
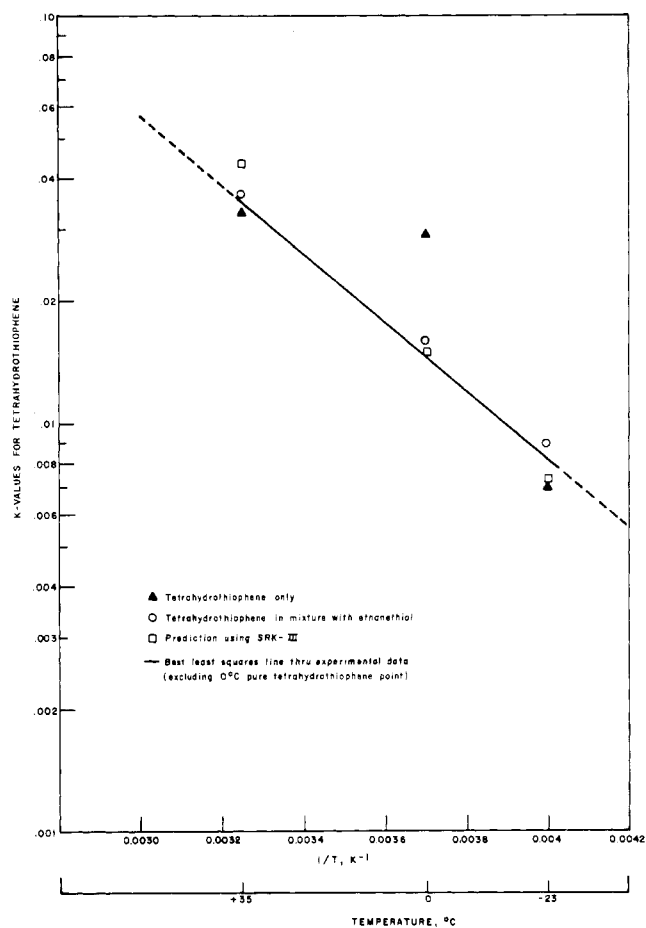

Figure 3. Theoretical and experimental K values for tetrahydrothiophene in propane as a function of the inverse of absolute temperature.

also observed during this study, especially with tetrahydrothiophene. Solubility problems were investigated by other workers (5) and found to be insignificant even at much higher concentrations. Therefore, the most likely source of problems in this study and those reported previously was the actual taking of the sample. For this reason, the valving/sampling system on the metal bomb was made as simple as possible. This also aided attainment of equilibrium by reducing the volume of gas that was not in intimate contact with the main vapor phase and by eliminating recesses that tend to hold small amounts of liquid which can interfere with vapor samples.

At the colder temperatures, samples took longer to reach equilibrium, as expected. However, once in equilibrium, they gave the most reproducible results, which was fortunate, since much less vapor could be extracted without affecting the system equilibrium significantly. In order to obtain an independent check on the validity of the vapor sampling technique, a separate experiment was conducted in which propane and odorant were charged to the bomb to give 5 ppm of ethanethiol and 5 ppm of

tetrahydrothiophene in near-saturated propane vapor (no liquid phase). The vapor was sampled through a septum by use of a glass syringe fitted with a hypodermic needle, the technique considered most prone to condensation of odorant. Analyzed by the techniques already described, the resulting peak areas did indeed correspond to a vapor concentration of 5 ppm for each odorant. This indicated that no condensation occurred with this vapor sample technique. Since this technique showed no measureable condensation, it was assumed the technique used at 35 °C, with its larger diameter pathways, would also yield valid concentrations.

The K values obtained for the three sample systems at three different temperatures are presented in Table I. As mentioned, these values are an average of replicate analyses and have a typical relative standard deviation of about 5%. As can be seen, very little, if any, experimentally significant difference is observed for the odorants in the mixture as compared to the single odorant samples. The one exception is the 0 °C tetrahydrothiophene-alone value which, although reproduced several times,

seemed out of line with both the mixture values and the values for tetrahydrothiophene at other temperatures. It is felt that this value is incorrect, but time and funding did not permit further investigation. The value obtained with the mixture is considered probably close to the correct value.

A plot of the experimental K values obtained for ethanethiol vs. the inverse of the absolute temperature yields a nominally straight line, as shown in Figure 2. Also included in the figure are values predicted by Hankinson et al. (3, 4) using the SRK-III (Soave-modified Redlich-Kwong (7, 8)) equation of state and a C_{12} value of 0.06. This constant is an interaction parameter necessary for the calculation, but arbitrarily selected for reasonable agreement with physical data and experimental results. The best least-squares fit to the data is shown and corresponds to the equation

$$\ln K = b + a/T \tag{1}$$

where a is -906 and b is 1.54, with an average absolute percent error of 7.9%.

A similar plot of K values for tetrehydrothiophene is shown in Figure 3. In this case, the predicted values are obtained for an interaction parameter value of 0.035. A least-squares fit of the experimental data using eq 1 gives values of -1953 and 2.998 for a and b, respectively, and an average absolute percent error of 8.5%, if one neglects the·0 °C tetrahydrothiophene-only point.

In both cases, the computer calculations gave surprisingly good agreement with the experimental values, especially considering the low concentration levels involved. Although the interaction parameter can be changed somewhat arbitrarily, the slopes agree quite well. Thus, it is felt that the described method provides a reliable means of determining K values for pure odorants in propane as well as mixtures. K values in these mixtures, while important in many commercial applications, could not be determined by a titration. The method is simple and inexpensive, yet yields quite reproducible and reliable results, with the main time consideration being the period between mixing and equilibrium.

Literature Cited

(1) deSouza, T. L. C., Lane, D. C., Bhatia, S. P., Anal. Chem., 47, 543 (1975).
(2) Hankinson, R. W., Wilson, G. M., Proc., Annu. Conv. Nat. Gas Process. Assoc., No. 53, 100 (1974).
(3) Hankinson, R. W., Estes, R. C., Coker, T. A., 68th Annual American Institute of Chemical Engineering, Los Angeles, Calif., Nov 17, 1975.
(4) Hankinson, R. W., private communication (computer calculations of K values for ethanethiol and tetrahydrothiophene).
(5) Jentoft, R. E., Olund, S. A., "Solubility of Odorants in Liquid Petroleum Gas", National Meeting of the American Chemical Society, Chicago, Ill., Aug 30–Sept 4, 1964.
(6) Prausnitz, J. M., Bazua, E., Proc., Annu. Conv., Nat. Gas Process. Assoc., No. 52, 31 (1973).
(7) Soave, G., Chem. Eng. Sci., 27, 1197 (1972).
(8) Soave, G., Chem. Eng. Sci., 28, 2268 (1973).
(9) Zudkevitch, D., Wilson, G. M., Proc., Annu. Conv., Nat. Gas Process. Assoc., 53, 101 (1974).

Aqueous Solubility of Polynuclear Aromatic Hydrocarbons

Donald Mackay* and Wan Ying Shiu

Department of Chemical Engineering and Applied Chemistry and Institute for Environmental Studies, University of Toronto, Toronto, Ontario M5S 1A4, Canada

The solubilities of 32 polynuclear aromatic hydrocarbons and indan have been measured in water at 25 °C. The results compare satisfactorily with the available literature values for ten of the compounds. The hydrocarbon infinite dilution coefficient is correlated with carbon number using a parabolic equation. Aqueous solubility can then be calculated directly for hydrocarbons which are liquid at 25 °C. For solid hydrocarbons the ratio of hydrocarbon solid fugacity to hypothetical subcooled liquid fugacity must be estimated. A suitable correlation is suggested.

In assessing the impact of spills and other emissions of oil in the aquatic environment, it is generally accepted that the more soluble monoaromatic or polynuclear aromatic hydrocarbons (PNA's) are likely to have the most significant toxic effects. Fortunately the monoaromatics such as benzene, toluene, and xylenes evaporate fairly rapidly and their concentration in the aqueous phase and thus their impact on aquatic biota may be considerably reduced. There is a possibility that the PNA's, being less volatile, will be retained longer in the aqueous phase and thus exhibit greater toxicity. Some PNA's have been implicated as carcinogens.

Aqueous solubility is a fundamental parameter in assessing PNA dissolution extent and rate and their persistence in the aquatic environment. The extent to which aquatic biota are exposed to a toxicant such as a PNA is largely controlled by the aqueous solubility. In addition, these solubilities are of thermodynamic interest in elucidating the nature of these highly nonideal solutions.

In this work the solubilities of 32 PNA's and indan have been measured in distilled water at 25 °C, and an attempt has been made to correlate the solubility as a function of molecular structure. This enables the solubility of other PNA's to be estimated with sufficient accuracy for environmental calculation purposes.

Experimental Section and Results

All the hydrocarbons used were of the highest grade commercially available and were obtained from Aldrich Chemicals, Eastman Kodak, or K and K Laboratories. They were used without further purification.

Saturated aqueous solutions were prepared by adding an excess quantity of hydrocarbon to doubly distilled water in 250-mL flasks with glass stoppers. The solution was stirred vigorously with a Teflon-coated magnetic bar for 24 h and subsequently settled at 25 °C for at least 48 h before analysis. In some cases the initial dissolution was done at higher temperatures to increase dissolution rate. The saturated aqueous solutions were decanted and filtered through a 5-μ Millipore filter to remove suspended particles. There is a risk that hydrocarbon may be removed from solution by adsorption on the glassware