Table III. Adjusted Values of Parameters C in Equation 1

System	C_1	C_2	C_3	C_4	σ/(J/mol)
Benzene–NMP (25°C)	−1989.8	410.5	−0.389	−292.4	5.38
Benzene–NMP (40°C)	−1956.3	273.7	−0.389	+64.239	5.46
NMP–Ethanolamine (25°C)	3168.5	−1602.2	1441.8	77.866	10
NMP–Ethanolamine (40°C)	3556.0	−1366.7	905.8	−114.07	8.1
Cyclohexane–NMP (25°C)	5443.0	44.028	3711.8	−1809.9	13.15

effect of molecular structure on excess properties of mixtures.

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Determination of Solubilities of Light Hydrocarbons in Di-2-ethylhexyl Sebacate by Saturation of a Gas-Liquid Chromatographic Column

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The solubilities of propane, isobutane, neopentane, and *cis*-2-butene in di-2-ethylhexyl sebacate at low concentrations have been determined by measuring the amount of hydrocarbon sample required to saturate all the liquid in a chromatographic column. The method does not depend upon the progress of a peak conforming to a particular mathematical model of the chromatographic process and therefore is generally applicable. The solubilities at 55°C were: propane 0.182, isobutane 0.090, neopentane 0.057, and cis-2-butene 0.045, expressed as (mol/cm^3 in gas)/(mol/cm^3 in liquid).

Numerous investigators have measured the solubility of volatile compounds in relatively nonvolatile compounds by gas–liquid chromatography *(4, 5, 6, 9)*. Newman and Prausnitz *(8)* have used the method to measure the solubility of volatiles in polymers.

The determinations of solubility have generally used ordinary isothermal analytical chromatographs. A column containing a known amount of nonvolatile liquid is prepared and installed in the chromatograph oven. Carrier gas flow is adjusted to a known rate and a pulse of volatile material is injected into the carrier stream. The times for the sample peak and for an air peak to appear at the detector are measured. The retention volume is calculated from these time measurements and used in other equations to deduce the solubility (or activity coefficient). The calculations are described by Kuchhal and Mallik *(7)* and Newman and Prausnitz *(8)*.

To the extent that the physical situation existing in the column is described by the equations, this method is sound and accurate. The principal limitations are that the solubility of the volatile compound follow Henry's law, that there be no absorption of volatile on the solid support, that mass transfer rates be relatively high, and that axial dispersion in the column not affect the position of the maxima of the peaks.

A convenient method which is not subject to these limitations, for determining the solubility of volatiles in nonvolatile compounds, is based on completely saturating the liquid of a chromatographic column with a volatile material. It has been used to determine the solubility of propane, isobutane, neopentane, and *cis*-2-butene in di-2-ethylhexyl sebacate.

Method and Apparatus

Figure 1 is a schematic diagram of the apparatus. A column (A), containing a known weight of di-2-ethylhexyl sebacate on the packing was prepared. The packing was prepared by dissolving the di-2-ethylhexyl sebacate in acetone, mixing the solution with the support in an evaporating dish and, with continuous stirring, evaporating off the acetone over a water bath. The packing was dried to constant weight in a vacuum oven at 100°C. The amount of di-2-ethylhexyl sebacate on the packing was determined by extracting a weighed sample of the packing with ether for 24 hr and drying the extracted packing to constant weight.

Flow-through type thermistor detectors (B,B') were mounted at the inlet and outlet of the column. Three gas streams (C,C',C'') measured by critical orifices (D,D',D'') were fed to the system continuously. Streams C and C' were pure carrier gas streams. Stream C'' was sample gas. Depending upon the position of a switch connected to solenoid valves E and E', either the carrier gas stream (C') or the sample gas stream (C'') was fed to the column, the other stream being vented. The sample gases were solutions of argon or one of the hydrocarbons in helium.

The pressure at the column outlet as indicated by absolute pressure manometer F was maintained constant by regulator G attached to surge tank H. The total flow through the column was maintained constant by regulator

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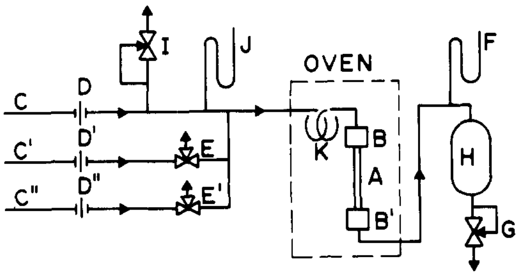

Figure 1. Arrangement of gas chromatograph

I, which bled off enough of the main carrier gas stream to keep the column inlet pressure as indicated by absolute pressure manometer *J* constant. A coil of tubing *K* was located in the oven to heat the gas stream to oven temperature before it entered the inlet detector, *B*. Further details of the components are given by Carter and Esterson *(2)*.

The outputs of the two detectors were displayed on a two-channel oscillographic recorder.

A sample gas mixture containing argon, which is negligibly soluble in di-2-ethylhexyl sebacate at the experimental conditions, was first used as sample gas. The switch was set so that the pure carrier gas entered the system and the sample gas was vented. After the detector outputs had stabilized, the switch was thrown so that sample gas (argon in helium) was fed to the system and the pure carrier steam (*C'*) was vented. When the sample gas reached the inlet detector, its output changed to a new steady-state value. Later on, when the sample gas had filled the column, a similar response was observed at the outlet detector. The difference in time responses of the detectors was a function of the gas flow required to fill the column void volume. The gas flow rate was kept low deliberately, so that the pressure drop through the column was low and gas partial pressures and the gas flow rate calculated at the mean of the inlet and outlet pressures could be used without significant error. The switch was then returned to its original position and the reverse responses were observed at the inlet and outlet detectors as the sample gas was purged from the system.

Next, a sample gas cylinder containing one of the hydrocarbons in solution was connected to the sample gas system. The solenoid valves were switched as before. The response of the outlet detector was longer delayed because it was not only necessary to fill the void volume with sample gas as above, but also to saturate the di-2-ethylhexyl sebacate with hydrocarbon at the solubility corresponding to the partial pressure of the hydrocarbon at the mean of the column total inlet and outlet pressures.

Calculation of Solubility from Detector Responses

In the development which follows, carrier gas is defined as pure helium; volatile refers to either argon which is not soluble in the liquid, or to hydrocarbon which is soluble; and sample refers to mixtures of carrier and volatile.

The inlet and outlet detectors measure the concentrations of volatile in the sample gas entering and leaving the column. The mass of volatile entering the column between time $t = 0$ and $t = \theta$ is

$$n_i(\theta) = \int_0^\theta F_i(t)c_{gi}(t)dt \tag{1}$$

The mass of volatile leaving the column in the same period is

$$n_o(\theta) = \int_0^\theta F_o(t)c_{go}(t)dt \tag{2}$$

The accumulation of volatile in the liquid and gas phases of the column in this period is

$$n_l(\theta) + n_g(\theta) = \int_0^\theta F_i(t)c_{gi}(t)dt - \int_0^\theta F_o(t)c_{go}(t)dt \tag{3}$$

If $t = 0$ is taken as the time the switch is thrown and $t = \theta$ is taken large enough so that the outlet detector has responded to the sample change and settled at a new steady state value, the liquid phase in the column is in equilibrium with the gas phase.

For argon $n_l(\theta) = 0$, so $n_g(\theta)$ for the column can be obtained by applying Equation 3 to the responses obtained with an argon sample mixture. For a hydrocarbon mixture of the same molar concentration $n_l(\theta) + n_g(\theta)$ is obtained from Equation 3 and $n_l(\theta)$ is calculated by difference.

$$\begin{aligned} n_l(\theta) = {} & \left[\int_0^\theta F_i(t)c_{gi}(t)dt - \int_0^\theta F_o(t)c_{go}(t)dt\right]_{\text{hydrocarbon}} \\ & - \left[\int_0^\theta F_i(t)c_{gi}(t)dt - \int_0^\theta F_o(t)c_{go}(t)dt\right]_{\text{argon}} \end{aligned} \tag{4}$$

The concentration of hydrocarbon in the liquid at equilibrium is calculated from the equation

$$c_l = \frac{\rho}{W} n_l(\theta) \tag{5}$$

The solubility, *H*, in concentration units (a form of the Henry's law constant) is

$$H = \frac{c_g}{c} \tag{6}$$

where c_g is the gas phase concentration calculated at the mean of the inlet and outlet pressures.

Since

$$c_g = \frac{p}{RT} \tag{7}$$

the constant *H'* relating partial pressure and liquid concentration is

$$H' = HRT = \frac{p}{c_l} \tag{8}$$

From its definition, the activity coefficient is

$$\gamma = p/xP_v = c_gRT/xP_v \tag{9}$$

Application of Equation 4 to obtain $n_l(\theta)$ provides a method for measuring gas solubilities which is independent of a mathematical model of the chromatographic process. However, it does require accurate measurement of inlet and outlet gas flow rates and accurate calibration of the detectors. For most real cases, these restrictions can be relaxed.

If the inlet and outlet flows may be considered constant, the concentration terms in Equation 4 may be normalized as follows:

$$\begin{aligned} n_l(\theta) = {} & \left[F_i(\theta)c_{gi}(\theta)\int_0^\theta \frac{c_{gi}(t)}{c_{gi}(\theta)}\,dt - F_o(\theta)c_{go}(\theta)\int_0^\theta \frac{c_{go}(t)}{c_{go}(\theta)}\,dt\right]_{\text{hydrocarbon}} \\ & - \left[F_i(\theta)c_{gi}(\theta)\int_0^\theta \frac{c_{gi}(t)}{c_{gi}(\theta)}\,dt - F_o(\theta)c_{go}(\theta)\int_0^\theta \frac{c_{go}(t)}{c_{go}(\theta)}\right]_{\text{argon}} \end{aligned} \tag{10}$$

Defining F_A and c_{gA} as the steady-state flows calculated at the mean of the inlet and outlet pressures gives

$$F_A c_{gA} = F_i(\theta) c_{gi}(\theta) = F_o(\theta) c_{go} \tag{11}$$

If the responses of the detectors are linear with concentration,

$$r_i(t) \propto c_{gi}(t) \tag{12}$$

and

$$r_o(t) \propto c_{go}(t) \tag{13}$$

Applying Equations 11, 12, and 13 to Equation 10 gives

$$n_l(t) = F_A c_{gA} \left\{ \left[\int_0^\theta \frac{r_i(t)}{r_i(\theta)} dt - \int_0^\theta \frac{r_o(t)}{r_o(\theta)} dt \right]_{\text{hydrocarbon}} - \left[\int_0^\theta \frac{r_i(t)}{r_i(\theta)} dt - \int_0^\theta \frac{r_o(t)}{r_o(\theta)} dt \right]_{\text{argon}} \right\} \tag{14}$$

The normalized inlet detector responses should be the equal for all sample gases, so Equation 14 becomes

$$n_l(\theta) = F_A c_{gA} \left\{ \left[\int_0^\theta \frac{r_o(t)}{r_o(\theta)} dt \right]_{\text{argon}} - \left[\int_0^\theta \frac{r_o(t)}{r_o(\theta)} dt \right]_{\text{hydrocarbon}} \right\} \tag{15}$$

Equation 15 should be applicable in most real cases. The sample must be sufficiently dilute to permit considering the inlet and outlet flows the same and the responses of the detectors must be known to be linear with concentration. Calibration of detector response with concentration is not required.

If the total response of the inlet and outlet detectors occurs over a very short period of time relative to time between the responses of the output detector with argon and hydrocarbon, the responses can be approximated by a unit step function. If the responses are unit step functions, Equation 15 can be written

$$n_l(\theta) = F_A c_{gA}(t_h - t_a) \tag{16}$$

where t_h and t_a are the times at which the outputs of the detectors underwent step changes.

Equation 4, 15, or 16 may be used to calculate $n_l(\theta)$, depending upon the restrictions which must be applied. The value of $n_l(\theta)$ obtained should then be substituted in Equation 5 to calculate the concentration of volatile in the liquid.

The method will obviously measure any volatile adsorbed on the support, so it is necessary to choose a support on which volatile is not adsorbed.

Experimental

Table I gives experimental conditions and equipment parameters for the measurements of the solubility of hydrocarbons in di-2-ethylhexyl sebacate. In Table II, the results are given as the Henry's law constants, H, the constants, H', which relate partial pressure to the liquid phase composition, and the activity coefficients at low concentration.

To validate the method, the Henry's law constants were also determined by saturating aliquots of di-2-ethylhexyl sebacate with the hydrocarbons at controlled temperatures and pressures and determining the weight increase of the liquid. These results, reported in Table II, agreed well with those obtained by the chromatographic method. The Henry's law constants were found to be independent of hydrocarbon partial pressure up to and including the highest partial pressures studied, which are given in Table II.

Table I. Equipment Parameters and Operating Conditions

Column dimensions. 0.46 cm i.d. × 30.5 cm long
Solid support. 3.185 grams 30–60 mesh Teflon 6
Detectors. VECO MX239 (Victory Engineering Corp., Union, N.J.)
Density of di-2-ethylhexyl sebacate. 0.891 g/cm^3 at 55°C
Di-2-ethylhexyl sebacate[a] in packing. 0.339 g
Oven temperature. 55°C
Vapor pressure of hydrocarbons (*1*)

Propane	14,100	Torr
Isobutane	5,840	Torr
Neopentane	3,050	Torr
cis-2-butene	3,720	Torr

Column inlet pressure. 782 torr
Column outled pressure. 760 torr
Mean column pressure. 771 torr
Total gas flow through column (F). 39.4 cm^3/min (55°C and 771 torr)
Sample gas flow. 39.4 cm^3/min (55°C and 771 torr)
Sample gas[b] concentrations. 1 mol % sample gas in helium

[a] Consolidated Electrodynamics Corp., Rochester, N.Y. [b] Matheson Co., Joliet, Ill.

Table II. Solubility Measurement

Hydrocarbons	Gas-liquid chromatography measurements: H, (mol/cm^3)$_g$ / (mol/cm^3)$_l$	Gas-liquid chromatography measurements: H', torr / (mol/cm^3)$_l$	Gas-liquid chromatography measurements: γ	Liquid saturation measurements: H, (mol/cm^3)$_g$ / (mol/cm^3)$_l$	Liquid saturation measurements: Maximum partial pressure, torr
Propane	0.182	3.723×10^{-6}	0.55	0.196	400
Isobutane	0.090	1.841×10^{-6}	0.66	0.088	287
Neopentane	0.057	1.353×10^{-6}	0.80	0.058	136
cis-2-Butene	0.045	0.92×10^{-6}	0.52	0.048	139

Since the sample feeds were dilute and the detector responses were rapid, Equation 16 was used to calculate $n_l(\theta)$ from the experimental results. Application of Equation 15 to the same responses gave identical results.

Discussion

The accuracy of the method, which does not rely on the chromatographic process being described by a particular mathematical model, has been demonstrated.

In the cases studied, the volatilities of the solutes were great enough that the sample gases could be made up as helium solutions in pressure cylinders. For less volatile solutes, sample gas might be obtained by bubbling pure helium through volatile liquid downstream of critical orifice D'' at controlled temperature.

Covitz and King (*3*) have recently pointed out the usefulness of gas–liquid chromatography for measuring the solubility of volatiles in polymers. They note, however, that the peak retention volume method did not permit them to explore high solute concentration ranges because of the limitation that Henry's law apply. The method of this paper should be particularly useful for high solute concentration measurements in polymers.

Nomenclature

c_g = concentration of volatile in gas phase, mol/cm^3
c_l = concentration of volatile in liquid phase, mol/cm^3
n = moles volatile, g-mol
p = partial pressure of volatile, torr

r = signal from detector, V
t = time, sec
x = mole fraction volatile in liquid
F = gas flow, cm^3/sec
H = Henry's law constant, $(\text{mol/cm}^3)_g/(\text{mol/cm}^3)_l$
H' = proportionality constant, torr/$(\text{mol/cm}^3)_l$
P_v = vapor pressure of hydrocarbon, torr
R = gas constant, 62361.0 torr-cm^3/sec
T = absolute temperature, K
V = volume of volatile dissolved in liquid, cm^3 vapor
W = weight of stationary phase in column, g

Subscripts

$_a$ = argon
$_A$ = average
$_g$ = gas phase
$_h$ = hydrocarbon
$_i$ = inlet detector
$_l$ = liquid phase
$_o$ = outlet detector

Greek Letters

γ = activity coefficient
ρ = density of stationary phase, g/cm^3
θ = upper time for integration, sec

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Vapor-Liquid Equilibrium of Methyl-*n*-Butylamine-Water

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Vapor-liquid equilibria are reported at 10°, 20°, 30°, and 40°C calculated by the total pressure method. Various thermodynamically consistent equations are examined for representing the results.

This work is part of a continuing study of hydrogen-bonding solutions involving amines, water, and alcohols. Previous work on various amine-water mixtures (*1, 3*) has shown them to be an interesting class with large excess functions, lower critical solution temperatures, where partial miscibility exists, and rather unusually shaped isothermal pressure-composition curves. In general, the excess free energy is poorly represented by the usual thermodynamically consistent polynomials and a large number of constants are necessary to obtain satisfactory agreement with the data.

Experimental

Total pressure-composition data were measured with a static apparatus that allows sample degassing without change in composition. Two samples can be run at once and pressures at up to six temperatures have been obtained in a day.

The apparatus consists of sample flasks, stopcocks, two manometers, and connecting glass tubing assembled on a frame with ball joints. The frame and apparatus, suspended in an aquarium water bath, can be rocked on its suspension to hasten equilibrium. The manometers are read through the plate glass with a cathetometer. Equilibrium, as indicated by steady pressure measurements, is usually reached in 10–15 min following stabilization of the temperature. When equilibrium has been obtained, the temperature may be increased and additional measurements obtained on the same samples. The apparatus and its operation have been completely described (*4*). Temperatures were controlled to within 0.01°C by a thermistor-activated proportional controller. Temperatures were measured with a calibrated glass thermometer graduated in 0.1°C and the reported values are believed to be accurate within 0.03°C. Pressures were measured to within 0.05 mm of Hg. The accuracy of the measurements is probably within 0.1–0.2 mm, although leaks, failure to obtain equilibrium, or contamination by stopcock grease may occasionally cause greater errors. The largest pressure error that could result in the reported data from a temperature deviation of 0.03°C is about 0.2 mm of Hg at 40°C. The manometer readings were corrected for temperature and gravity. Vapor pressures of pure water were taken from Lange's Handbook (*5*).

The amine was distilled on a Stedman column at high reflux and a fraction boiling within 0.1°C was used. The fraction showed a single peak on a gas chromatograph.

Chemical analysis of the liquid phase was by acid titration of the amine, except above 90% amine by weight, where gas chromatography was employed. These methods gave amine concentrations within 1 part in 250 to 500. The low water concentrations are accurate to at least 1 mol %.

Calculation of Vapor–Liquid Equilibrium

Vapor compositions were not measured but were calculated by the total pressure method, in which pressure-liquid composition data are integrated with the Gibbs-Duhem equation. The latter was expressed in the form

$$\ln \gamma_2 = -\frac{x_1}{x_2} \ln \gamma_1 + \int_0^{x_1} \frac{\ln \gamma_1}{x_2^2}\, dx_1 \qquad (1)$$

By use of an integration formula, this equation was solved simultaneously at each increment with

$$P = P_1^\circ \Phi_1 \gamma_1 x_1 + P_2^\circ \Phi_2 \gamma_2 x_2 \qquad (2)$$

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