Processes, Academic Press, New York (1971).

Randolph, A. D., and S. K. Sikdar, "Effect of a Soft Impeller Coating on the Net Formation of Secondary Nuclei," *AIChE J.*, **20**, No. 2, 410 (1974).

———, "Survival of Secondary Crystal Nuclei of K_2SO_4," Preprints Vol. 1, p.A5-3, GVC/AIChE Joint Meeting, Munich (1974).

Randolph, A. D., and S. K. Sikdar, "Creation and Survival of Secondary Nuclei: The K_2SO_4-Water System," in press (1975).

Rosen, H. M., "Importance of Slip Velocity in Determining Growth and Nucleation Kinetics in Continuous Crystallization," *AIChE J.*, **20**, No. 2, 388 (1974).

———, and H. M. Hulburt, "Continuous Vacuum Crystallization of Potassium Sulfate," *Chem. Eng. Progr. Symp. Ser. No. 11*, **67**, 18 (1971).

Sikdar, S. K., "Secondary Nucleation Mechanisms and Kinetics in a Continuous-Flow, Seeded Crystallizer," Ph.D. dissertation, Univ. Ariz., Tucson (1975).

Sung, C. Y., G. R. Youngquist, and J. Estrin, "Secondary Nucleation by Fluid Shear," Preprints Vol. 1., p.A5-2, GVC/AIChE Joint Meeting, Munich (1974).

Wang, M. L., and J. Estrin, Dept. of Chemical Engineering, Clarkson College of Technology, Potsdam, New York, Private Communication (1974).

Youngquist, G. R., and A. D. Randolph, "Secondary Nucleation in a Class II System: Ammonium Sulfate-Water," *AIChE J.*, 18, 421 (1972).

Manuscript received May 9, 1975; revision received September 3 and accepted September 4, 1975.

Solubility of Gases and Liquids in Molten Polystyrene

Experimental solubility data have been obtained for sixteen organic solutes in molten polystyrene by a gas chromatographic procedure for temperatures from 408° to 503°K and pressures to 4 atm. The effects of diffusion and adsorption of the solute on the substrate were considered. The Henry's law constants resulting from this study and those obtained by other investigators were related to the reduced temperature. The effect of pressure on the Henry's law constants is also discussed, and a relationship is presented for the heat of solution.

LEONARD I. STIEL
and
DANIEL F. HARNISH

Allied Chemical Corporation
Specialty Chemicals Division
Buffalo, New York

SCOPE

Solubility values of gases and liquids in molten polystyrene are required in several important applications. For example, in the extrusion process for the production of polystyrene foam, an expansion agent is injected into the polymer at an elevated temperature and pressure and subsequently released at a lower temperature and pressure. An important physical variable influencing the quality and cost of the foam is the solubility of the agent at the initial and final stages of extrusion.

For molten polystyrene, solubility data have previously been reported for gases at elevated pressures and for liquids at low pressures. An examination of the solubilities from the various sources revealed some inconsistencies, and a need was established for additional data, particularly for substances with values intermediate to those of R-22 and *n*-pentane. Therefore, in the present study, solubility measurements have been obtained for sixteen organic solutes, and the available data have been utilized to develop a generalized method for the calculation of this property.

CONCLUSIONS AND SIGNIFICANCE

For amorphous polyethylene, Stern et al. (1969) found that the available solubility data could be represented by a linear relationship between the log of the Henry's law constant and $(T_c/T)^2$. In this study, a similar approach has been found to be applicable for the solubility of gases and liquids in molten polystyrene. The Henry's law constants obtained from various sources have to be initially reduced to a common basis.

The Henry's law constants presented in this study enable the estimation of solubilities for a number of substances for which data were previously not available. The correlation of the available data enables the calculation of solubilities for additional substances. The effect of pressure on the solubilities can be estimated by use of the relationships discussed.

The chromatographic method is a useful procedure for the determination of solubilities in polymers. The correlation of the data aids in the analysis of the measurements.

For molten polystyrene, the available solubility data include the values of Newitt and Weale (1948) for hydrogen, nitrogen, carbon dioxide, and ethylene for 403° to 463°K and 80 to 300 atm.; Lundberg et al. (1962, 1963) for methane for 373° to 461°K and 80 to 325 atm.; and Durrill and Griskey (1966) for nitrogen, carbon dioxide, helium, argon, and chlorodifluoromethane (R-22) at 462°K and pressures to 20 atm. These investigators utilized high pressure sorption experiments in which solubility and diffusivity data were simultaneously obtained. Duda and Vrentas (1968) obtained solubilities and diffusivities for *n*-pentane at 1 atm and 413° to 443°K by the use of a quartz spring sorption apparatus. Similar measurements were made by Duda et al. (1973) for ethylbenzene for

433° to 451°K and approximately 1 atm.

Recently, a gas chromatographic technique has found considerable utility for the determination of solubilities in polymers. Chromatographic measurements of solubilities in molten polystyrene at low pressures were obtained by Brockmeier et al. (1972) for benzene and ethylenebenzene at 393°K and ethylbenzene at 453°K, by Newman and Prausnitz (1972) for a number of soluble organic liquids for 423° to 473°K, and by Covitz and King (1972) for organic liquids for 397° to 483°K. In this study a similar procedure has been utilized to determine solubilities in molten polystyrene for a number of organic solutes.

DETAILS OF EXPERIMENTAL INVESTIGATION

The experimental measurements were conducted with a Varian Aerograph Autoprep Model A-700 chromatograph equipped with a thermal conductivity detector. The polystyrene was coated onto Fluoropak-80 support by dissolution from chloroform solution, and the coated materials were packed into 0.64 cm copper tubing. The percent polymer on the support was determined from the weights of each constituent charged, and the amount of packing in the column from the initial and final weights of the tubing. The column was placed into the chromatograph and the temperature, pressure, and carrier gas flow rate adjusted to the desired level. The column temperature was measured with a thermocouple attached to the column in the oven. This procedure was tested by placing thermocouples at various locations between the inlet and outlet of the column and was determined to be accurate to within 1°C.

The pressures of the helium carrier gas at the column inlet and detector outlet were controlled with needle valves. The inlet and outlet pressures were measured with small gauges. The flow rate at 1 atm was measured at the outlet of the system with a soap-bubble flowmeter. For liquids, a sample of approximately 0.2 μl was charged with a 10 μl syringe. Gaseous solutes were charged with a gas sampling apparatus, and the quantity injected depended on the pressure of the sample and the amount of time the valve was opened. The output of the detector was monitored with a recorder. The retention time for the injected solute to reach the detector was determined with a stopwatch as the time at which a maximum peak height was obtained on the recorder. Reference retention times were also measured for the column conditions of each run by the injection of air with the syringe for liquid samples, or by the injection of nitrogen with the gas sampling apparatus for gaseous solutes.

For each run, the specific retention volume V_g was calculated from the weight of polymer W, the measured flow rate Q, and the difference in retention times for the solute and the reference gas (Newman and Prausnitz, 1972) as

$$V_g = \frac{Q(t_g - t_r)\ 273.2}{\overline{P}\ W\ T_F} \qquad (1)$$

where T_F is the flowmeter temperature. The average pressure in the column $\overline{P}$ is calculated from the relationship

$$\overline{P} = 2/3\ P_o \left[\frac{(P_i/P_o)^3 - 1}{(P_i/P_o)^2 - 1} \right] \qquad (2)$$

where P_i is the inlet pressure and P_o the outlet pressure. By assuming ideal gas behavior, the Henry's law constant K_p is obtained from Equation (1) as

$$1/K_p = \frac{V_g^0}{P_1} = V_g \qquad (3)$$

where P_1 is the partial pressure of the solute in the gas phase, and V_g^0 is the solubility expressed as cubic centimeters of solute per gram of polymer at 273°K and 1 atm.

The columns which were prepared had the following characteristics:

Column Number	Column Length, cm	% Polymer (Fluoropak-80 substrate)
1	24	13.12
2	71	2.02
3	35	4.76
4	71	4.85

In order to test the effect of the substrate, a 35 cm column was also prepared with no polymer coating and a 71 cm column with 4.78% polymer and glass beads for the substrate. For column 1, the polystyrene utilized was supplied by Sinclair-Koppers Company and had a number average molecular weight of 115,000 and a wide molecular weight distribution of components. For the other columns, the polystyrene utilized was Pressure Chemical Company's Special Polystyrene Standard with $\overline{M_N} = 110{,}000$ and a very narrow molecular weight distribution.

EXPERIMENTAL RESULTS

Solubilities were measured with the various columns for R-22, trichlorofluoromethane (R-11), dichlorodifluoromethane (R-12), chlorofluoromethane (R-31), trichlorotrifluoroethane (R-113), methyl chloride, methylene chloride, chloroform, propane, isobutane, *n*-pentane, *n*-hexane, *n*-heptane, benzene, toluene, cyclopentane, and cyclohexane. The temperatures ranged from 408° to 503°K and pressures from 1 to 4 atm (101.325 to 405.3 N/m^2).

The chromatographic method enables the rapid determination of solubilities, but in order to obtain accurate results, diffusional and adsorption effects must be considered. The experimental solubilities for column 1, which was short in length and had a high coverage ratio (gram polymer per gram substrate), were in general lower than expected, particularly at low temperatures. Therefore, in subsequent runs longer columns with lower coverage ratios were employed to minimize the effect of diffusion. For these columns, the pressure drop required for reasonable flow rates are larger, adding to the experimental uncertainty.

The previous chromatographic measurements of solubilities in molten polystyrene were obtained by Brockmeier et al. (1972) with 47 cm long columns, low coverage ratios, and Chromasorb-W as the substrate; by Newman and Prausnitz (1973) with 24 cm long columns, various coverage ratios, and Fluoropak-80 as the substrate; and by Covitz and King (1972) with columns 1 m long, high coverage ratios, Chromasorb-P substrates, and polystyrenes with various molecular weight distributions. Brockmeier et al. (1972) found no dependence on flow rate for a 1% loading of polystyrene, with some dependence for a 5% loading. Newman and Prausnitz performed measurements at varying flow rates for each coverage ratio and extrapolated the results linearly to zero flow rate. Lichtenthaler et al. (1974) have subsequently suggested that a quadratic extrapolation should be employed.

In this study, measurements were made at varying flow rates with column 4 for the fluorocarbons and for propane, isobutane, and *n*-pentane for temperatures from 408° to 503°K. The calculated Henry's law constants were extrapolated to zero flow rate at each temperature to obtain the limiting values of $1/K_p$. Typical results are shown in Figure 1 for R-113. For a given coverage ratio, the extent of the variation with flow rate is dependent on both the solubility and diffusivity of the solute in the polymer.

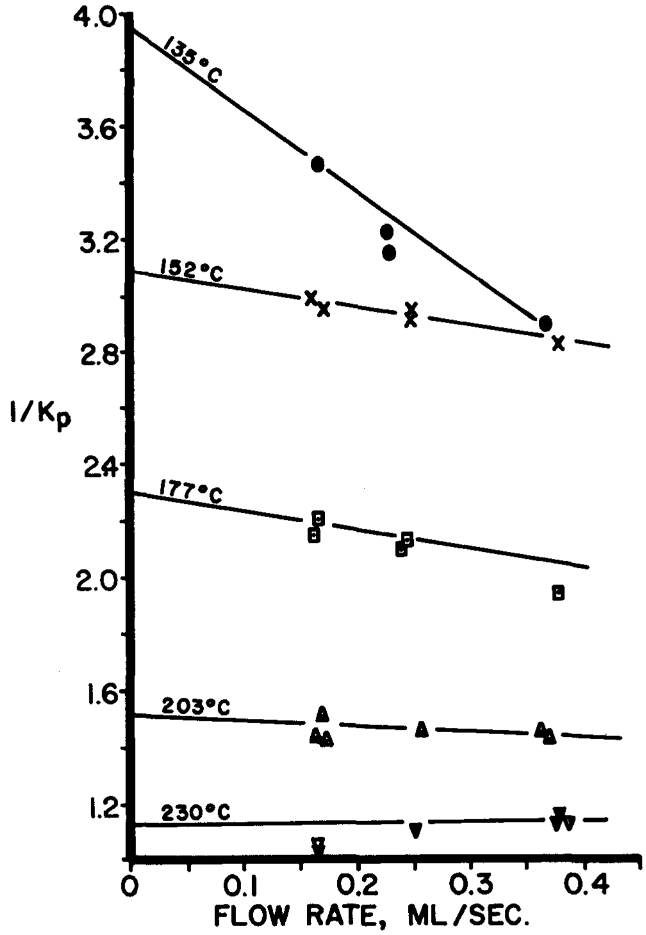

Fig. 1. Relationship between $1/K_p$ and flow rate for *R*-113.

In the treatment of the experimental measurements, the possibility of adsorption of the solute on the substrate resulting in high solubilities must also be considered. It has been suggested (Newman and Prausnitz, 1973) that the experimental solubilities are independent of coverage ratio if this ratio is greater than 0.05, the value used in most of the runs of this study. The solubilities obtained for the second column with a lower coverage ratio were in general higher than those obtained with the other columns. Newman and Prausnitz (1972) accounted for adsorption effects by plotting the limiting solubilities at zero flow rate against the reciprocals of the corresponding coverage ratios and by extrapolating to zero. In the present study, an extensive analysis of this type was not performed because of the considerable uncertainty resulting from double extrapolations of the data.

Adsorption contributions to the solubilities were studied by the use of a 35 cm column with Fluoropak-80 substrate and no polymer coating. All of the solutes had positive retention time differences for this column, with the differences increasing with decreasing temperatures. Some adjustments of the experimental solubilities were made on the basis of these values, but it was difficult to obtain reproducible results for gaseous solutes with this column. Measurements were also made with a column 71 cm long with glass beads as the substrate and a coverage ratio of approximately 0.05. For this column, adsorption effects were not present, but diffusional contributions were enhanced greatly. The specific retention times obtained with this column had to be extrapolated to zero flow rate even for highly soluble liquids. The results of these tests enabled the most suitable data for each substance to be favored in the analysis of the measurements.

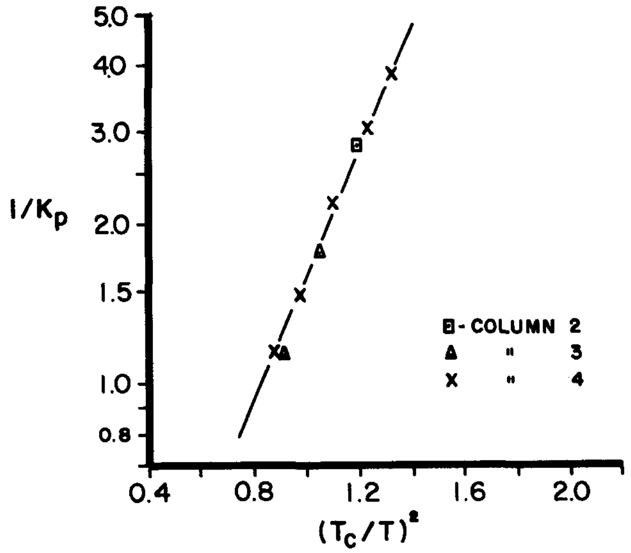

Fig. 2. Relationship between $1/K_p$ and $(T_c/T)^2$ for *R*-11.

TABLE 1. EXPERIMENTAL VALUES OF $1/K_p$

Substance	408°K	423°K	448°K	473°K	498°K
R-11	3.85	3.02	2.09	1.55	1.17
CH_2Cl_2	—	5.20	3.35	2.21	—
C_6H_6	—	13.10	7.75	4.93	3.40
C_7H_8	—	21.9	12.70	7.60	—
R-12	1.12	0.94	0.70	0.56	0.45
R-22	0.94	0.81	0.64	0.53	0.44
R-31	2.01	1.65	1.20	—	—
C_3H_8	0.90	0.78	0.62	0.51	0.43
i-C_4H_{10}	—	1.20	0.86	0.65	0.52
n-C_5H_{12}	3.35	2.60	1.80	1.28	0.98
R-113	—	3.50	2.33	1.65	1.22
n-C_6H_{14}	—	4.40	2.80	1.93	1.47
n-C_7H_{16}	—	—	4.80	3.12	2.18
CH_3Cl	—	1.70	1.30	—	—
C_5H_{10}	—	—	3.05	—	—
$CHCl_3$	—	—	3.20	—	—
C_6H_{12}	—	—	—	—	2.72

For gaseous solutes, the solubility in molten polystyrene is low, and measurements were obtained only for a coverage ratio of approximately 0.05. Another source of experimental uncertainty for these substances is that some changes in the results were detected with differences in the charging conditions. The amount of gaseous solute injected was determined by both the pressure of the gas sample and the length of time of injection. Accurate results could be obtained for these solutes only if the sample and reference gas were charged in exactly the same manner.

For each substance, the data for the various columns and conditions were plotted to obtain a linear relationship between the log of $1/K_p$ and $(T_c/T)^2$, as shown in Figure 2 for R-11. From these plots, interpolated values of $1/K_p$ were determined for each substance (if possible) at 408°, 423°, 448°, 473°, and 498°K and are presented in Table 1. The experimental solubilities are considered to be accurate to within approximately 10%.

CORRELATION OF EXPERIMENTAL DATA

Durrill and Griskey (1969) showed that the available solubility data for gases in molten polystyrene and other polymers at 461°K could be represented in terms of a linear relationship between the log of the Henry's law

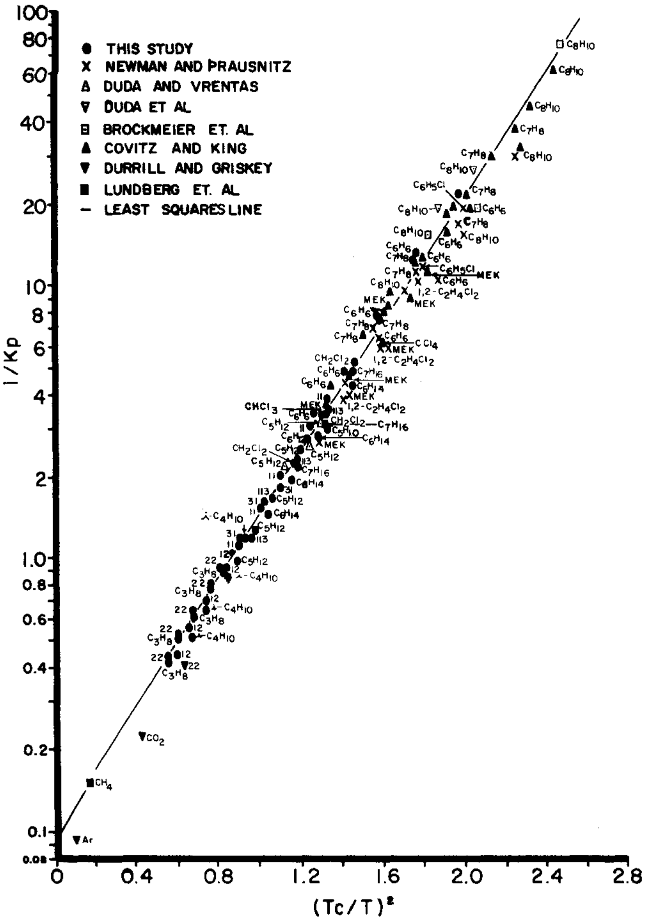

Fig. 3. Relationship between ln $(1/K_p)$ and $(T_c/T)^2$ for polystyrene.

constant and either the Lennard-Jones force constant or critical temperature of the solute. For amorphous polyethylene, Stern et al. (1969) found that the available solubility data for a wide range of solutes and temperatures could be represented as a linear relationship between the log of the Henry's law constant and $(T_c/T)^2$. In this study, a similar approach has been found to be applicable for the solubility of gases and liquids in molten polystyrene.

For liquid solutes at low pressures, the results of chromatographic measurements are usually reported in terms of an activity coefficient at infinite dilution γ_1. This activity coefficient is related to K_p defined in Equation (3), as follows (Everett et al., 1961):

$$K_p = \frac{\gamma_1 P_1^s M_1}{22{,}414} e^{[(P_1^s/RT)(B_{11}-v_1) - (\bar{P}/RT)(2B_{12}-B_{22}-\bar{v}_1)]} \tag{4}$$

where M_1 is the molecular weight of the solute, and P_1^s and v_1 are the vapor pressure and molar volume of the saturated liquid. The partial molar volume of the solute at infinite dilution $\bar{v}_1$ can be approximated as v_1. In Equation (4), B_{11} is the second virial coefficient of the solute, B_{22} the virial coefficient of the carrier gas, and B_{12} the interaction virial coefficient.

Brockmeier et al. (1972), Newman and Prausnitz (1972), and Covitz and King (1972) reported their results in terms of the infinite dilution activity coefficient. Covitz and King (1972) neglected the exponential term in Equation (4), which is reasonable at low pressures. Newman and Prausnitz (1972) neglected the second term in the exponential part, which enhanced the contribution of the first term involving the vapor pressure. In this study, values of K_p were calculated by the use of relationships consistent with those utilized by the investigators to determine the reported activity coefficients from the experimental retention volumes.

The Henry's law constants obtained by chromatographic measurements for all the sources, including the data of this study, are in substantial agreement and result in a linear relationship when plotted as log $1/K_p$ vs. $(T_c/T)^2$, as shown in Figure 3. The experimental values of Newman and Prausnitz (1972) and Covitz and King (1972) show some negative deviations at low temperatures, possibly due to diffusional effects, but are in general agreement with the indicated relationship. The solubilities obtained by Duda and Vrentas (1968) for pentane and by Duda et al. (1973) for ethylbenzene with a quartz spring sorption apparatus at approximately atmospheric pressure are also in agreement with the relationship of Figure 3. Although the chromatographic measurements obtained in this study for substances of low solubility such as gases are of less certain reliability, the Henry's law constants for these solutes are, in general, consistent with the relationship obtained for the more soluble liquids.

In order to relate the solubility data for gases at elevated pressures with the values for liquid solutes at low pressures, the variation of the Henry's law constant with pressure must be considered. The effect of pressure can be expressed as

$$f_1 = K_f^{(0)} e^{(\bar{v}_1 P/RT)} V_g^0 \tag{5}$$

where f_1 is the fugacity of the solute in the gas phase, and $K_f^{(0)}$ is the Henry's law constant corrected to zero pressure. Most of the chromatographic measurements were obtained at approximately atmospheric pressure, and the values of $1/K_p$ are slightly lower than the corresponding values of $1/K_f^{(0)}$.

For a pure gaseous solute in contact with the polymer at moderate pressures, the fugacity required in Equation (5) can be represented as

$$f_1 = P\, e^{(B_{11}P/RT)} \tag{6}$$

Procedures for the estimation of $\bar{v}_1$ for gaseous solutes have been presented by Lyckman et al. (1965). Since $1/K_p$ represents the ratio V_g^0/P at 1 atm, the following relationship can be obtained from Equations (5) and (6) for this case:

$$1/K_p = \left(\frac{V_g^0}{P}\right) e^{[(\bar{v}_1 - B_{11})(P-1)/RT]} \tag{7}$$

For the data of Lundberg et al. (1963) for methane at 461°K, the values of $1/K_p$ calculated from Equation (7) and the experimental values of (V_g^0/P) for pressures to 315 atm are consistent with the linear relationship of Figure 3. For the results of Durrill and Griskey (1966) for pressures to 20 atm, the calculated values of $1/K_p$ are lower than those resulting from the linear relationship. However, the experimental data for this source exhibit considerable scatter, and the calculated values for some points are in closer agreement with this relationship. The values for the data of Newitt and Weale (1948) which are of questionable reliability (Durrill and Griskey, 1966) also deviate considerably from the linear relationship. For these substances, the solubilities are very low, and it cannot be established conclusively from the results of this study that a linear relationship is applicable for $(T_c/T)^2 < 0.6$.

For all the sources, values of ln $(1/K_p)$ for $(T_c/T)^2 > 0.6$ were related to $(T_c/T)^2$ by a least-squares procedure. The resulting relationship is

$$\ln (1/K_p) = -2.338 + 2.706\ (T_c/T)^2 \qquad (8)$$

For 109 points utilized to establish Equation (8), the average percent error between experimental and calculated values was 7.53%. For the data of this study, the average error was 6.13% for 56 points. For the data of Covitz and King (1972), the average error was 8.0% for 26 points and 8.29% for 18 points from the data of Newman and Prausnitz (1972). It was found that if a linear term in (T_c/T) is also included, about the same overall error is obtained, and the coefficient of this term is small. In Table 2, values of the Henry's law constants obtained in this study for benzene, toluene, *n*-pentane, and R-22 are compared with the corresponding values obtained in other investigations and with those calculated from Equation (8).

DISCUSSION

The chromatographic method to obtain solubilities in molten polymers requires extensive analysis to obtain reliable results. For each substance, a particular column will result in optimum measurements. Thus, for a substance of small molecular size and high solubility, a high coverage ratio should be used, while for a solute of large size and limited solubility, meaningful results can only be obtained with low coverage ratios, even if adsorption effects are significant. For gaseous solutes, modifications of the experimental procedure would improve the accuracy of the results. The correlation of the available data for all the substances aids in the analysis of the chromatographic measurements and enables the prediction of the solubility of substances for which data are not available.

Equation (8) enables the calculation of solubilities for nonpolar or slightly polar substances at moderate pressures from the reduced temperature of the solute. The effect of pressure on the solubility can be estimated through Equation (5). The relationship for the temperature variation of K_p is

$$\frac{d(\ln K_p)}{dT} = \frac{L}{RT^2} \qquad (9)$$

where L is the heat absorbed in the vaporization of 1 mole of solute from the solution at constant temperature and atmospheric pressure. From Equations (8) and (9), the following relationship is obtained for the range of applicability of Equation (8):

$$L = 45.025\ (T_c^2/T) \quad \text{(Joule/mole)} \qquad (10)$$

Equation (10) indicates that the heat of solution is strongly dependent on critical temperature and varies inversely with the temperature.

Most of the solubility data utilized for the development of Equation (8) were obtained for polystyrene samples with a number average molecular weight of approximately 100 000. Covitz and King (1972) found that the Henry's law constant decreases slightly with increasing molecular weight of the polystyrene.

TABLE 2. COMPARISON OF HENRY'S LAW CONSTANTS FROM DIFFERENT SOURCES

Substance	T°K	$1/K_p$	Reference
Benzene	448°	7.40	Covitz and King, 1972
		6.50	Newman and Prausnitz, 1972
		7.75	*
		6.75	†
Toluene	448°	12.40	Covitz and King, 1972
		11.09	Newman and Prausnitz, 1972
		12.70	*
		10.83	†
n-Pentane	423°	2.69	Duda and Vrentas, 1968
		2.60	*
		2.69	†
R-22	462°	0.41	Durrill and Griskey, 1966
		0.575	*
		0.545	†

* This study.
† Calculated from Equation (8).

ACKNOWLEDGMENT

John Wilczynski constructed the columns and obtained most of the chromatographic measurements. Earl A. E. Lund helped in setting up the experimental equipment.

NOTATION

B_{11} = second virial coefficient of solute, cm^3/g mole
B_{22} = second virial coefficient of carrier gas, cm^3/g mole
B_{12} = interaction virial coefficient for solute and carrier gas, cm^3/g mole
f_1 = fugacity of solute, atm
$K_f^{(0)}$ = Henry's law constant corrected to zero pressure
K_p = Henry's law constant defined in Equation (3)
$1/K_p$ = solubility at a total pressure of approximately 1 atm, cm^3(273°K, 1 atm)/g atm
L = heat of vaporization of solute from solution, Joule/mole
$\overline{M_N}$ = number average molecular weight
MW_1 = molecular weight of solute
P = pressure, atm
$\overline{P}$ = average pressure in column, atm, defined in Equation (2)
P_1 = partial pressure of solute in gas phase, atm
P_1^s = vapor pressure of solute, atm
P_i = pressure at inlet to column, atm
P_o = pressure at outlet of column, atm
Q = flow rate in flowmeter at atmospheric pressure, cm^3/min
R = gas constant
T = temperature, °K
T_c = critical temperature, °K
T_f = temperature in flowmeter, °K
t_g = retention time of solute in column, min.
t_r = retention for reference gas in column, min.
v_1 = molar volume of liquid solute at saturation, cm^3/g mole
$\bar{v}_1$ = partial molar volume of solute in polymer at infinite dilution, cm^3/g mole
V_g = specific retention volume, cm^3/g, corrected to 273°K and the average column pressure
V_g^0 = specific retention volume, cm^3(273°K, 1 atm)/g
W = weight of polymer in column, g
w_1 = weight ratio of solute to polymer
γ_1 = activity coefficient of solute at infinite dilution, defined in Equation (4)

LITERATURE CITED

Brockmeier, N. F., R. W. McCoy, and J. A. Meyer, "Gas Chromatographic Determination of Thermodynamic Properties of Polymer Solutions. I. Amorphous Polymer Systems," *Macromolecules*, **5**, 464 (1972).

Covitz, F. H., and J. N. King, "Solute Absorption into Molten Polystyrene," *J. Polymer Sci.*, **10**, A-1, 689 (1972).

Duda, J. L., and J. S. Vrentas, "Diffusion in Atactic Polystyrene Above the Glass Transition Point," *ibid.*, **6**, A-2, 675 (1968).

Duda, J. L., G. K. Kimmerly, W. L. Sigelko, and J. W. Vrentas, "Sorption Apparatus for Diffusion Studies with Molten Polymers," *Ind. Eng. Chem. Fundamentals*, **12**, 133 (1973).

Durrill, P. L., and R. G. Griskey, "Diffusion and Solution of Gases in Thermally Softened or Molten Polymers: Part I.

Development of Technique and Determination of Data," *AIChE J.*, 12, 1147 (1966).

———, "Diffusion and Solution of Gases into Thermally Softened or Molten Polymers: Part II. Relation of Diffusivities and Solubilities with Temperature, Pressure, and Structural Characteristics," *ibid.*, 15, 106 (1969).

Everett, D. H., and C. T. H. Stoddart, "The Thermodynamics of Hydrocarbon Solutions from G.L.C. Measurements Part I. Solutions in Dinonyl Phthalate," *Trans. Faraday Soc.*, 57, 746 (1961).

Lichtenthaler, R. N., D. D. Liu, and J. M. Prausnitz, "Polymer-Solvent Interactions from Gas-Liquid Chromatography with Capillary Columns," *Macromolecules*, 7, 565 (1974).

Lundberg, J. L., M. B. Wilk, and M. J. Huyett, "Estimation of Diffusivities and Solubilities from Sorption Studies," *J. Polymer Sci.*, 57, 275 (1962).

———, "Sorption Studies Using Automation and Computation," *Ind. Eng. Chem. Fundamentals*, 2, 37 (1963).

Lyckman, E. W., C. A. Eckert, and J. M. Prausnitz, "Generalized Reference Fugacities for Phase Equilibrium Thermodynamics," *Chem. Eng. Sci.*, 20, 685 (1965).

Newitt, D. M., and E. W. Weale, "Solution and Diffusion of Gases in Polystyrene at High Pressures," *J. Chem. Soc. (London)*, 1541 (1948).

Newman, R. D., and J. M. Prausnitz, "Polymer-Solvent Interactions from Gas-Liquid Partition Chromatography," *J. Phys. Chem.*, 76, 1492 (1972).

———, "Polymer-Solvent Interaction from Gas-Liquid Chromatography," *J. Paint Technol.*, 45, No. 585, 33 (1973).

Stern, S. A., J. T. Mullhaupt, and P. J. Gareis, "The Effect of Pressure on the Permeation of Gases and Vapors through Polyethylene. Usefulness of the Corresponding States Principle," *AIChE J.*, 15, 64 (1969).

Manuscript received January 30, 1975; revision received September 17, and accepted October 16, 1975.

Experimental Study of the Residence Time Distribution in Plasticating Screw Extruders

Experimental residence time distribution functions for the liquid and solids conveying processes by a screw conveyer and for the polymer in a plasticating extruder were obtained by using a radioactive tracer technique. A comparison was made between the experimental results and several theoretical models available for melt extrusion and mixing processes.

DAVID WOLF
and
DON H. WHITE
Department of Chemical Engineering
University of Arizona
Tucson, Arizona 85721

SCOPE

The objective of this study was to obtain experimental data on the residence time distribution (RTD) of polymers in a plasticating extruder. The results were then compared with theoretical models derived for melt extrusion and other mixing unit operations. RTD functions were also obtained for liquid and solids conveying in screw conveyers. A special technique was developed for that purpose by using radioactive material as the tracer. The experiments were performed employing two methods. By the first method the tracer was preactivated and then injected, while by the second method the tracer was first injected and then samples of the output were activated. The effect of several parameters, such as temperatures of the screw and its rotational speed, were also investigated. The information obtained by the RTD function is of interest for the performance of the extruder, especially when time dependent processes take place in the extruder or in the screw conveying process.

CONCLUSIONS AND SIGNIFICANCE

The plasticating extruder is probably the most widely used unit operation in the polymers industry. The mixing conditions, flow patterns, and residence time distribution (RTD) in a plasticating extruder have significant effects on the product, especially when polymers sensitive to heat are extruded or when good mixing of additives is required. For the use of extruders as polymerization reactors, as it is recently being considered, the knowledge of the residence time distribution is even more important. Therefore, an experimental study on the residence time distribution of the polymer material in a single screw plasticating extruder was made and compared with the limited theory available to date. Additional experiments were made with solids conveying and with liquid conveying by the extruder screw so as to be able to model the plasticating extruder and its various zones as closely as possible.

The experiments for the determination of the RTD were made by using a radioactive tracer, and two different techniques were used for the output analysis. Both techniques were found applicable for the RTD determination in the plasticating extrusion process. The tracer used was a master batch of 1% manganese dioxide in polyethylene which in the first method was irradiated in a nuclear reactor before it was injected into the extruder, whereas in the second method it was injected without being irradiated. The post irradiation method is more time consuming but enables one to test the extruder also in cases where radioactive material cannot be handled at the location of the extruder.

David Wolf is with the Ben Gurion University of the Negev, Beer Sheva, Israel, and Weizmann Institute of Science, Rehovot, Israel.