

Correlation of the Solubility of Volatile Liquids in Molten Polymers

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Synopsis

The solubility of volatile liquids at infinite dilution (i.e., in the Henry's law region) in poly(vinyl acetate) (PVAc) and polystyrene (PS) at elevated temperatures has been correlated by plotting $\ln(1/K_p)$ against $(T_c/T)^2$, where T_c is the critical temperature of the solute and K_p is Henry's constant at temperature T and a total pressure of approximately at 1 atm, defined as $P_1 = K_p V_1^0$, where P_1 is the partial pressure of the solute in the vapor phase and V_1^0 is the solubility (cm^3 solute per g polymer at 273.2 K and 1 atm). For this correlation, we have used experimental data available in the literature for 16 solutes covering 81 data points for PVAc and 17 solutes covering 82 data points for PS. We have calculated values of $1/K_p$ from the literature data reported in terms of the retention volume V_g^0 , weight-fraction Henry's constant H_1 , and activity coefficient at infinite dilution Ω_1^∞ . We have made the following observations: (1) for PVAc, $\ln(1/K_p) = -1.564 + B(T_c/T)^2$; and (2) for PS, $\ln(1/K_p) = -2.028 + B(T_c/T)^2$. In both cases, we found that values of B , the slope in the $\ln(1/K_p)$ versus $(T_c/T)^2$ plots, vary with the acentric factor ω of the solutes. It has been found that, in both PVAc and PS at the same value of ω , values of B for slightly polar aromatic solutes are larger than those for nonpolar aliphatic solutes. Further, in PS at the same value of ω , values of B are smaller for strongly polar solutes than for slightly polar solutes, whereas in PVAc the opposite trend holds. This observation may be interpreted as that the solubility of strongly polar solutes in a polar polymer (e.g., PVAc) is greater than that of slightly polar and nonpolar solutes, whereas the solubility of strongly polar solutes in a nonpolar polymer (e.g., PS) is less than that of slightly polar solutes but greater than that of nonpolar solutes. The dependence of B on ω , observed in this investigation, is at variance with the correlations reported by Tseng, Lloyd, and Ward for PVAc and by Stiel and Harnish for PS.

BACKGROUND

Information on the solubility of volatile liquids in molten polymers is very important, for instance, to the design of equipment for polymer processing operations, such as polymer devolatilization and thermoplastic foam processes. In general, the collection of solubility data of volatile liquids in molten polymers is very time consuming. Therefore, it is highly desirable to have a predictive capability when only a limited amount of data is available.

About a decade ago, utilizing 109 data points of various gases and organic solutes for polystyrene (PS) at elevated temperatures, Stiel and Harnish¹ obtained the expression

$$\ln \frac{1}{K_p} = A + B \left(\frac{T_c}{T} \right)^2 \quad (1)$$

where T_c is the critical temperature of the solute, and K_p is a Henry's constant at a total pressure of approximately at 1 atm defined as $P_1 = K_p V_1^0$,

where P_1 is the partial pressure of the solute in the vapor phase and V_1^0 is the solubility (cm^3 solute per g polymer at 273.2 K and 1 atm). They reported that, independent of the type of solutes considered, eq. (1) with $A = -2.338$ and $B = 2.706$ correlates the experimental data with an average error of 7.53%. If this is true, eq. (1) would be very useful for predicting the solubility of gases and organic solutes in PS, having only the critical temperatures of the gases or solutes.

Very recently, Stiel et al.² have attempted to find whether a correlation similar to eq. (1) could be found for predicting the solubility of organic solutes in low-density polyethylene (LDPE), high-density polyethylene (HDPE), or polyisobutylene (PIB) at elevated temperatures. For the attempt, they used the literature data reported in terms of the specific retention volume V_g^0 , weight-fraction Henry's constant H_1 , activity coefficient at infinite dilution Ω_1^∞ , Flory-Huggins interaction parameter χ , or data obtained from high-pressure sorption experiments. They have found that eq. (1) correlates experimental data with values of B varying with the type of solute. Specifically, it was found that B in eq. (1) is correlatable linearly with the acentric factor ω ($\omega > 0.08$) of the solutes, as follows:

$$B = 2.057 + 1.438\omega \quad (2)$$

for molten LDPE with the value of $A = -1.451$ for 27 nonpolar solutes covering 115 data points, and

$$B = 1.790 + 1.568\omega \quad (3)$$

for PIB with the value of $A = -1.347$ and $\omega > 0.15$ for 18 solutes covering 148 data points. The average errors of values of $1/K_p$ calculated from eqs. (1) and (2) for LDPE and those calculated from eqs. (1) and (3) for PS are 6.0 and 8.9%, respectively.

Tseng et al.³⁻⁵ also have attempted to correlate the solubility data of various organic solutes in poly(vinyl acetate) (PVAc), PIB, and LDPE at elevated temperatures. They have reported³ that eq. (1) correlates the solubility data of organic solutes in PVAc with three different sets of numerical values of A and B ; namely, (1) $A = -2.010$ and $B = 2.693$ for 21 strongly polar solutes covering 95 data points, (2) $A = -1.579$ and $B = 2.200$ for 5 aromatic solutes covering 44 data points, and (3) $A = -2.491$ and $B = 2.175$ for 16 nonpolar and nonaromatic solutes covering 53 data points. In other words, they reported different values of intercept A and slope B in the $\ln(1/K_p)$ versus $(T_c/T)^2$ plots for the three different groups of solutes considered but the same values of A and B for a number of solutes within each group. No attempt was made to relate the slope B to a structural parameter(s) of the solutes.

Utilizing 118 data points of 13 solutes for PIB, Tseng et al.⁴ obtained a *single* line using the expression

$$\ln \frac{P_c}{100K_p} = A + B \left(\frac{T_c}{T} \right)^2 \quad (4)$$

with $A = -2.754$ and $B = 2.372$, where P_c is the critical pressure of the

solute. They have claimed that it was necessary to multiply $1/K_p$ by P_c in order to obtain the correlation. Their observation is at variance with the results of Stiel et al.,² eqs. (1) and (3).

In a separate paper,⁵ Tseng et al. have reported again that eq. (4) correlates the solubility data of 33 organic solutes covering 165 data points for molten LDPE, with $A = -2.523$ and $B = 2.411$. In other words, they suggested the use of a *single* least-squares line, independent of the type of solute, in the $\ln(P_c/100K_p)$ versus $(T_c/T)^2$ plots for predicting the solubility of organic solutes in molten LDPE. This observation is again at variance with the results of Stiel et al.,² eqs. (1) and (2).

The purpose of this paper is to report our more recent investigation on the correlation of the solubility of organic solutes at infinite dilution in PVAc and PS at elevated temperatures.

REDUCTION OF EXPERIMENTAL DATA

In the present investigation, we have used the experimental data available in the literature, dealing with the solubility of organic solutes at infinite dilution in poly(vinyl acetate) and polystyrene at elevated temperatures. Values of $1/K_p$ were calculated from reported data for the specific retention volume V_g^0 , weight-fraction Henry's constant H_1 , and activity coefficient at infinite dilution Ω_1^∞ , using the procedure described in a previous paper by Stiel et al.² Owing to the limitations of space, we shall not describe again the procedures employed. It should be pointed out that most of the data available in terms of the V_g^0 , H_1 , or Ω_1^∞ were taken using gas-liquid chromatography, and such experimental techniques generate solubility data in the Henry's law region. We have excluded from our consideration the solubility data for gases and for organic solutes at finite concentrations for the following reasons. First, the solubility data of organic solutes at finite concentrations must be extrapolated to infinite dilution (i.e., approaching zero concentration), in order for us to use them, together with those data already available at infinite dilution.

TABLE I
Average Errors Between Experimental and Calculated Values of $1/K_p$ for Poly(vinyl Acetate)

Solute	No. points	T (°C)	Slope B^a	ω	Average % error	References
<i>n</i> -Octane	3	90-120	1.689	0.394	2.08	8
<i>n</i> -Heptane	4	100-140	1.603	0.351	2.94	7, 8
Toluene	9	80-200	2.205	0.257	3.57	6, 7, 8
Benzene	9	80-200	2.195	0.212	4.00	6, 7, 8
Cyclohexane	4	100-140	1.690	0.213	7.00	7, 8
Carbon tetrachloride	4	90-135	1.994	0.194	4.24	8, 10
Chloroform	8	80-175	2.476	0.216	3.49	6, 8, 10
Vinyl acetate	4	125-200	2.372	0.340	7.61	9
Methyl ethyl ketone	6	125-200	2.426	0.329	4.10	7, 9
Acetone	6	125-200	2.274	0.309	5.56	7, 9

^aWith a common intercept, $A = -1.564$ in eq. (1).

TABLE II
Average Errors Between Experimental and Calculated Values of $1/K_p$ for Poly(vinyl Acetate)^a

Solute	Slope B^b	ω	Average % error
<i>n</i> -Nonane	1.726	0.444	1.86
<i>n</i> -Decane	1.810	0.490	2.20
<i>n</i> -Undecane	1.879	0.530	2.18
<i>n</i> -Dodecane	1.899	0.562	8.01
Cyclohexane	1.687	0.213	0.35
<i>n</i> -Butylcyclohexane	1.766	0.362	1.28
Benzene	2.187	0.212	0.40
<i>n</i> -Butylbenzene	2.218	0.392	0.59

^aTemperature was 125, 135 and 145°C. Number of points = 3.

^bWith a common intercept, $A = -1.564$ in eq. (1).

Source: Data from Reference 11.

However, extrapolation inevitably introduces additional errors of unknown magnitude. Second, almost all experimental data for gases that are available in the literature were taken at finite concentrations, using high-pressure sorption methods, and therefore, the use of such data also requires extrapolation, which would inevitably introduce additional errors. Moreover, we have learned from a previous investigation² that an additional parameter or parameters may be required to correlate the solubility data of gases of low molecular weight (e.g., nitrogen, carbon dioxide, and ethylene) in molten polymers, using an expression similar in type to eq. (1).

TABLE III
Average Errors Between Experimental and Calculated Values of $1/K_p$ for Polystyrene

Solute	No. points	T (°C)	Slope B^a	ω	Average % error	References
<i>n</i> -Hexadecane	3	183, 193, 203	2.786	0.742	1.19	13
<i>n</i> -Tetradecane	3	183, 193, 203	2.693	0.679	2.21	13
<i>n</i> -Dodecane	3	183, 193, 203	2.534	0.562	1.03	13
<i>n</i> -Decane	7	183, 193, 203	2.420	0.490	3.87	12, 13
<i>n</i> -Heptane	4	140-200	2.217	0.351	5.83	12
<i>n</i> -Butylbenzene	3	183, 193, 203	2.665	0.362	0.89	13
Ethylbenzene	7	140-200	2.564	0.301	2.66	12, 14
Toluene	7	140-200	2.558	0.257	2.64	12, 14
Chlorobenzene	3	150, 175, 200	2.528	0.249	0.76	14
Benzene	10	140-200	2.533	0.212	5.20	12, 13, 14
<i>n</i> -Butylcyclohexane	3	160, 170, 180	2.372	0.392	0.84	13
Cyclohexane	10	140-200	2.256	0.212	12.28	12, 13, 14
Cyclohexanone	3	150, 175, 200	2.661	0.443	4.69	14
Methyl ethyl ketone	3	150, 175, 200	2.410	0.329	0.98	14
Acetonitrile	3	150, 175, 200	2.181	0.321	4.61	14
Dioxane	7	140-200	2.469	0.288	4.43	12, 14
1,2-Dichloroethane	3	150, 175, 200	2.447	0.286	4.35	14

^aWith a common intercept, $A = -2.028$ in eq. (1).

In the present investigation, we have utilized the solubility data of 16 organic solutes covering 81 data points for PVAc and 17 solutes covering 82 data points for PS. In general, the data from different sources have average errors greater than those from a single source, and therefore we have decided to first correlate solubility data from different sources and then compare the correlation with that obtained using a single source. Table I lists 10 solutes for PVAc from five different sources,⁶⁻¹⁰ Table II lists 8 solutes for PVAc from a single source,¹¹ and Table III lists 17 solutes for PS from three different sources.¹²⁻¹⁴ All three tables list the number of data points utilized and the range of temperatures considered.

In general, the experimental data from different sources have different degrees of error. Therefore, before proceeding to correlate the solubility data from different sources, we first checked the consistency of the data, by plotting $\ln(1/K_p)$ against $(T_c/T)^2$ for all the solutes considered from each source. When we found that the data from a particular source has values of $1/K_p$ consistently too large or too small compared with those from the rest of

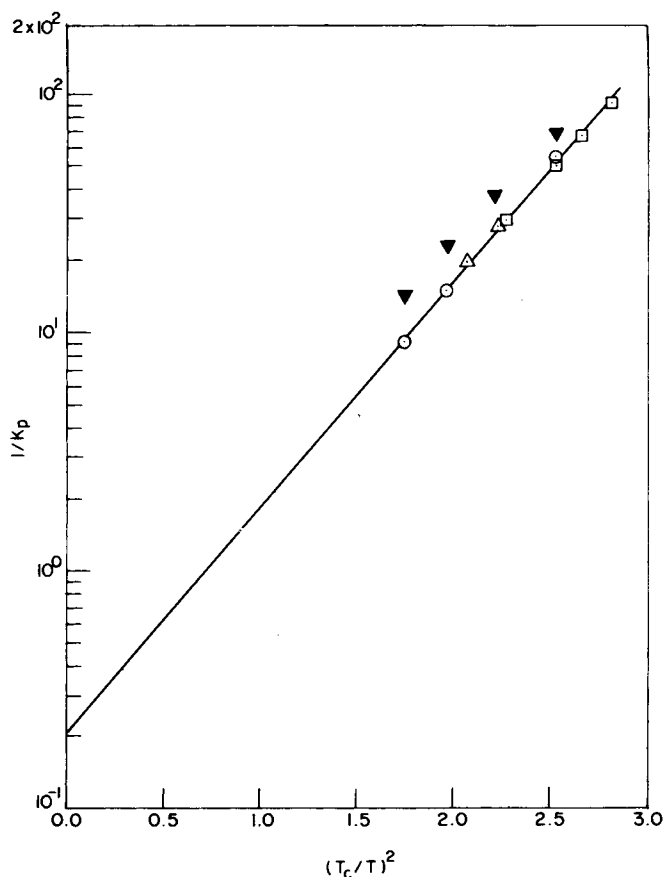


Fig. 1. $\ln(1/K_p)$ versus $(T_c/T)^2$ for toluene in PVAc. (Data are from ○ Ref. 6; ▲ Ref. 7; ◻ Ref. 8; ▼ Ref. 15.)

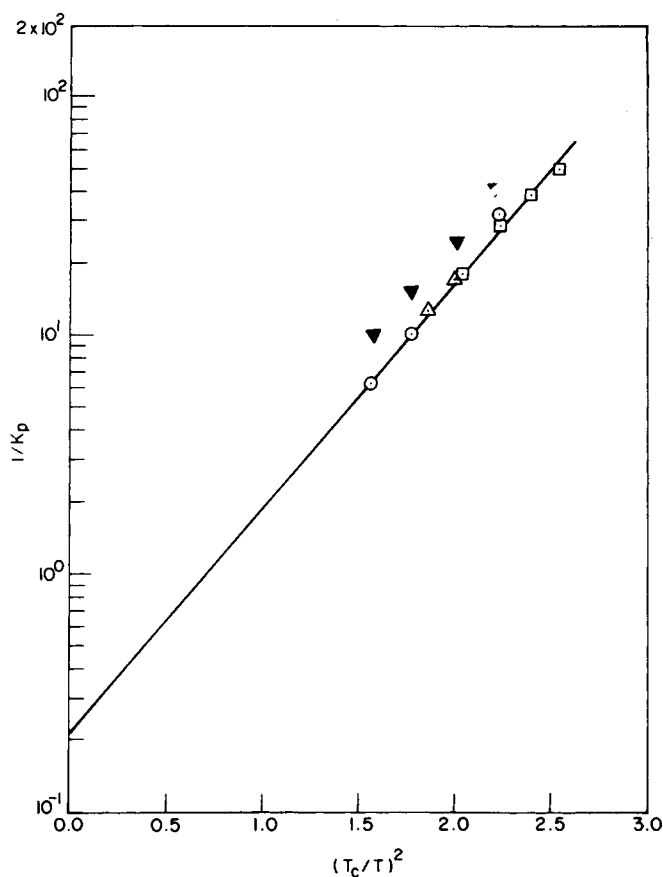


Fig. 2. $\ln(1/K_p)$ versus $(T_c/T)^2$ for benzene in PVAc. (Data are from \circ Ref. 6; Δ Ref. 7; \square Ref. 8; \blacktriangledown Ref. 15.)

the sources, we have excluded the data source from further consideration. To illustrate this approach, plots of $\ln(1/K_p)$ versus $(T_c/T)^2$ are given in Figure 1 for toluene, in Figure 2 for benzene, and in Figure 3 for chloroform in PVAc. It is seen clearly that the data of Newman and Prausnitz¹⁵ have consistently low values of $1/K_p$ compared with those from three other sources, and therefore, we have excluded their data from our consideration in correlating the solubility data for PVAc. We have found a similar situation while analyzing solubility data for PS. Figure 4 gives plots of $\ln(1/K_p)$ versus $(T_c/T)^2$ for benzene, Figure 5 for toluene, and Figure 6 for cyclohexane in PS. It is seen in Figures 4 to 6 that the data of Gunduz and Dincer¹⁶ show consistently low values of $1/K_p$ compared with those from other sources, and therefore we have excluded their data from consideration in correlating the solubility data of organic solutes in PS. This preliminary screening of data has prevented confusion that otherwise might have occurred when we examined the correlation obtained and, more importantly, has improved the quality of correlation.

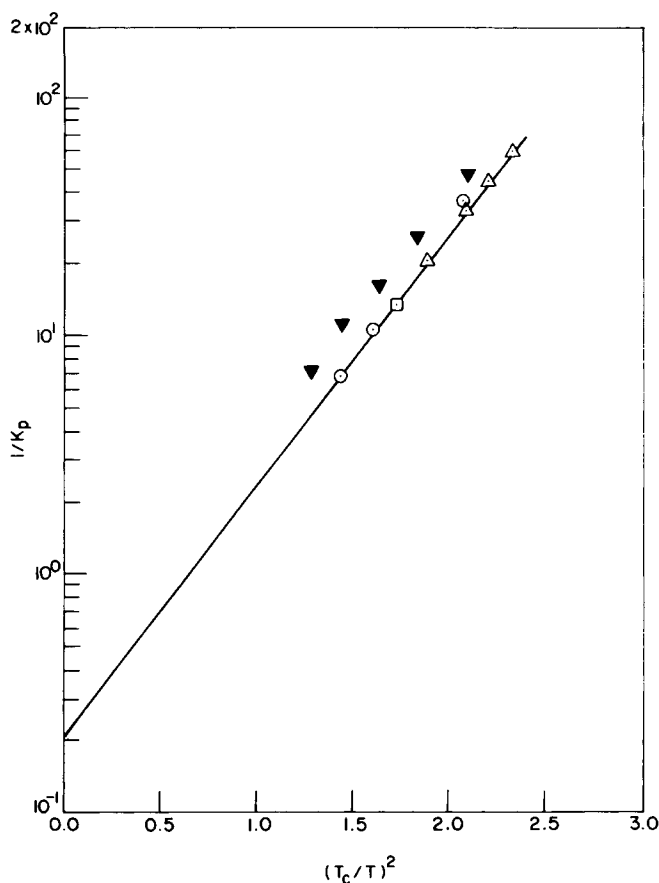


Fig. 3. $\ln(1/K_p)$ versus $(T_c/T)^2$ for chloroform in PVAc. (Data are from ○ Ref. 6; △ Ref. 8; □ Ref. 10; ▼ Ref. 15.)

RESULTS AND DISCUSSION

Correlation of the Solubility of Organic Solutes in Poly(vinyl Acetate)

Figure 7 gives plots of $\ln(1/K_p)$ versus $(T_c/T)^2$ for PVAc, prepared from the solubility data from five different sources (see Table I) for four nonpolar solutes (cyclohexane, *n*-heptane, *n*-octane, and carbon tetrachloride), three slightly polar solutes (benzene, toluene, and chloroform), and three strongly polar solutes (acetone, vinyl acetate, and methyl ethyl ketone) from five different sources (see Table I). Before drawing least-squares lines through the data points for each solute, we first applied linear regression analysis to the data points for each solute from individual sources, obtained intercepts for all solutes, and then took an average of the intercepts. The average value of the intercept for the 10 solutes covering 54 data points was found to be -1.564 . Least-squares lines were then drawn for all the solutes using a common intercept, -1.564 , at $(T_c/T)^2 = 0$. As may be seen in Figure 7, the solubility

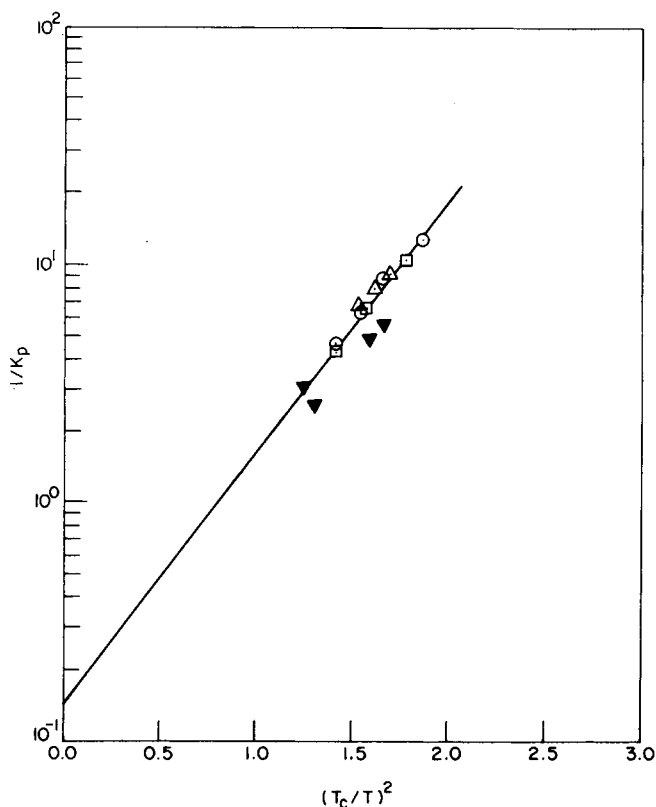


Fig. 4. $\ln(1/K_p)$ versus $(T_c/T)^2$ for benzene in PS. (Data are from \odot Ref. 12; \triangle Ref. 13; \square Ref. 14; \blacktriangledown Ref. 16.)

data of the 10 solutes may be represented by eq. (1), but with different values of B . Table I gives values of B determined from least-squares analysis using eq. (1), and the average percentage of error of values of $1/K_p$ calculated from eq. (1) for each solute. Note in Table I that the average error of values of $1/K_p$ for the 10 solutes using the common intercept is 4.46%. We have also determined the average percentage of error of values of $1/K_p$ using different values of intercept for each solute and found it to be 2.61%. It is concluded that the difference in the average error between 4.46% for the use of a common intercept and 2.61% for the use of separate intercepts for the 10 different solutes is insignificant for all intents and purposes. Therefore, we have decided to use the common intercept in pursuing further correlation.

Utilizing the solubility data of seven solutes from a single source,¹¹ listed in Table II, and with the common intercept -1.564 , the same as that for the 10 solutes listed in Table I, we have prepared plots of $\ln(1/K_p)$ versus $(T_c/T)^2$ in Figure 8. It is seen clearly in Figure 8 that each solute has a different slope, showing a trend very similar to that given in Figure 7. The average percentage errors for values of $1/K_p$ for each solute, plotted in Figure 8, are listed in Table II. It can be concluded from Tables I and II that the average error from a single source is definitely smaller than that from multiple sources. It is encouraging to observe in Table I and II that slope B for benzene and slope B

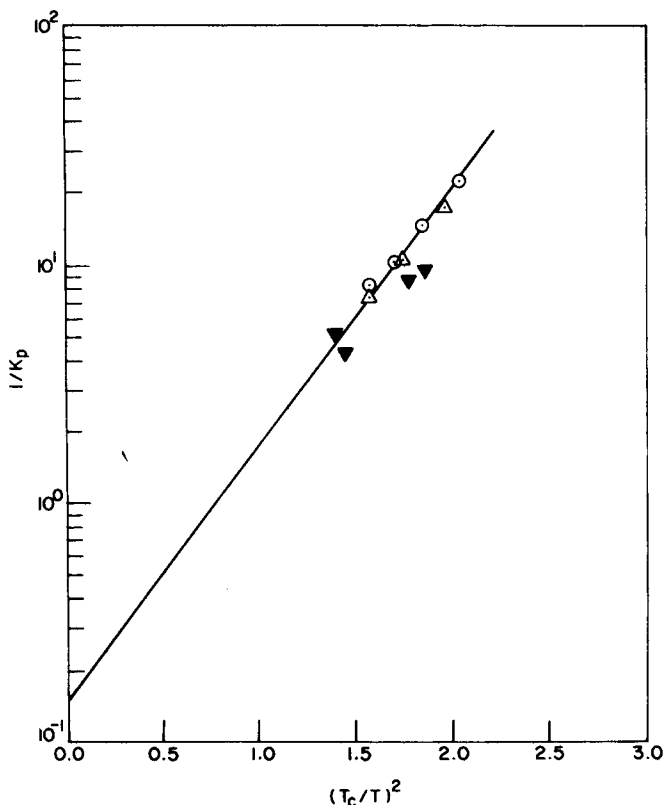


Fig. 5. $\ln(1/K_p)$ versus $(T_c/T)^2$ for toluene in PS. (Data are from \odot Ref. 12; \triangle Ref. 14; \blacktriangledown Ref. 16.)

for cyclohexane from a single source is almost the same as those from multiple sources.

Having observed that the slope B of $\ln(1/K_p)$ versus $(T_c/T)^2$ plots varies with the type of solute, we proceeded to examine whether we could correlate values of B to the acentric factor ω of the solutes. Plots of B versus ω are given in Figure 9. In Tables I and II we have listed values of the acentric factor ω for the solutes considered for PVAc. The acentric factors were taken from Reid et al.¹⁷ In reference to Figure 9, the following observations are worth noting. (1) For the nonpolar n -alkanes, values of B increase linearly with ω . (2) At the same value of ω , the aliphatic cyclic compounds (i.e., n -butylcyclohexane and cyclohexane) have values of B larger than the n -alkanes. There is also an increasing trend of B with increasing ω but with a slope much smaller than that for the n -alkanes. (3) At the same value of ω , values of B for the slightly polar aromatic solutes (benzene, toluene, and n -butylbenzene) are larger than those for the nonpolar aliphatic solutes, and values of B increases linearly with ω . (4) At the same value of ω , the strongly polar solutes (methyl ethyl ketone, acetone, and vinyl acetate) have much larger values of B than the slightly polar aromatic solutes and nonpolar aliphatic solutes, but there is no definite trend seen between B and ω for the polar solutes. (5) Carbon tetrachloride, which is considered nonpolar, has a

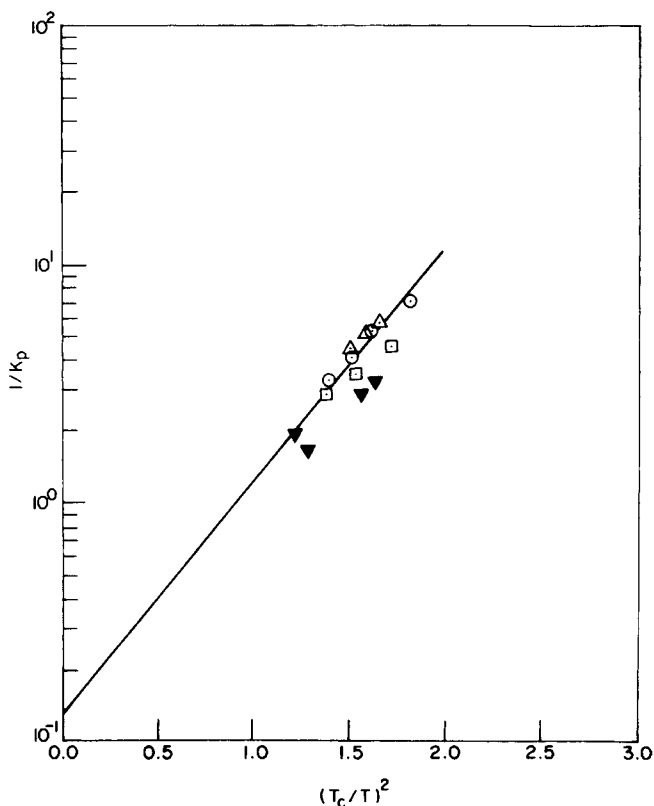


Fig. 6. $\ln(1/K_p)$ versus $(T_c/T)^2$ for cyclohexane in PS. (Data are from \odot Ref. 12; \triangle Ref. 13; \square Ref. 14; \blacktriangledown Ref. 16.)

value of B larger than the other nonpolar solutes considered, and chloroform, which is considered slightly polar, has the largest value of B of all the 16 solutes considered.

In their recent publications^{4,5} that dealt with the solubility of organic solutes in PIB and LDPE in the molten state, Tseng, et al. have claimed that eq. (4) gave a better correlation than eq. (1), and that it yielded a *single* least-squares line (i.e., a single value of B), independent of the type of solute. Their observations are at variance with the results of Stiel et al.² in that it was observed, for PIB and LDPE, that the multiplication of $1/K_p$ by P_c did not improve the quality of correlation obtained by eq. (1). Moreover, the use of either eq. (1) or (4) gave rise to values of B that vary with the type of solute that is, the values of B were correlated with the acentric factor ω . Therefore, in this study, we have investigated whether the use of eq. (4) can indeed improve the quality of correlation over the use of eq. (1), utilizing the same solubility data as those used in Figure 7.

Figure 10 gives plots of $\ln(P_c/100K_p)$ versus $(T_c/T)^2$ for PVAc, prepared with the solubility data of the 10 solutes covering 54 data points. In drawing least-squares lines through the data points in Figure 10, we have used the same procedure as described above in reference to Figure 7; that is, a common

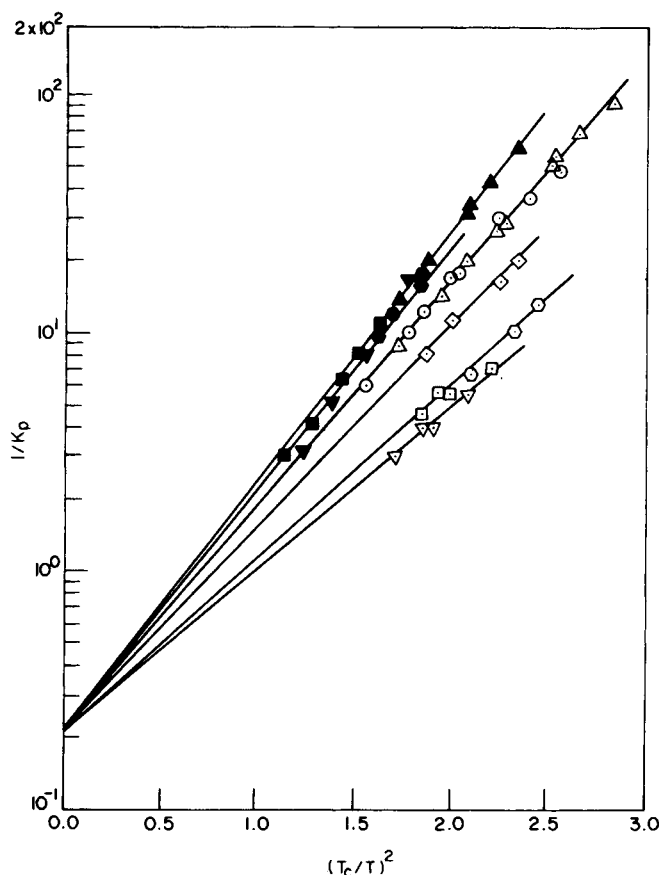


Fig. 7. $\ln(1/K_p)$ versus $(T_c/T)^2$ for organic solutes in PVAc. \circ benzene⁶⁻⁸, Δ toluene⁶⁻⁸, \square cyclohexane^{7,8}, ∇ *n*-heptane^{7,8}, \diamond *n*-octane⁸, \diamond carbon tetrachloride^{8,10}, \blacktriangle chloroform^{8,8,10}, \bullet methyl ethyl ketone^{7,9}, \blacksquare acetone^{7,9}, \blacktriangledown vinyl acetate.⁹

intercept, -2.579 , was used by averaging the intercepts obtained for each solute. Table IV gives a summary of values of B and the average percentage of error of values of $P_c/100K_p$ calculated from eq. (4). The following observations may be made on the quality of the correlation displayed in Figure 10. (1) A comparison of Figure 10 with Figure 7 indicates that the multiplication of $1/K_p$ by P_c makes the slopes of the least-squares lines spread farther apart than the use of $1/K_p$. This can also be observed by a comparison of the numerical values of B given in Tables I and IV. (2) For the 10 solutes considered, the average error of values of $P_c/100K_p$ calculated from eq. (4) is 4.84%, whereas the average error calculated from eq. (1) is 4.46%. This observation led us to conclude that the use of eq. (4) yields a quality of correlation that is poorer than that obtained with the use of eq. (1).

It should be mentioned at this juncture that we failed to understand how, when using eq. (4), Tseng et al.^{4,5} were able to obtain a *single* least-squares line passing through all the data points of several solutes for LDPE and PIB.

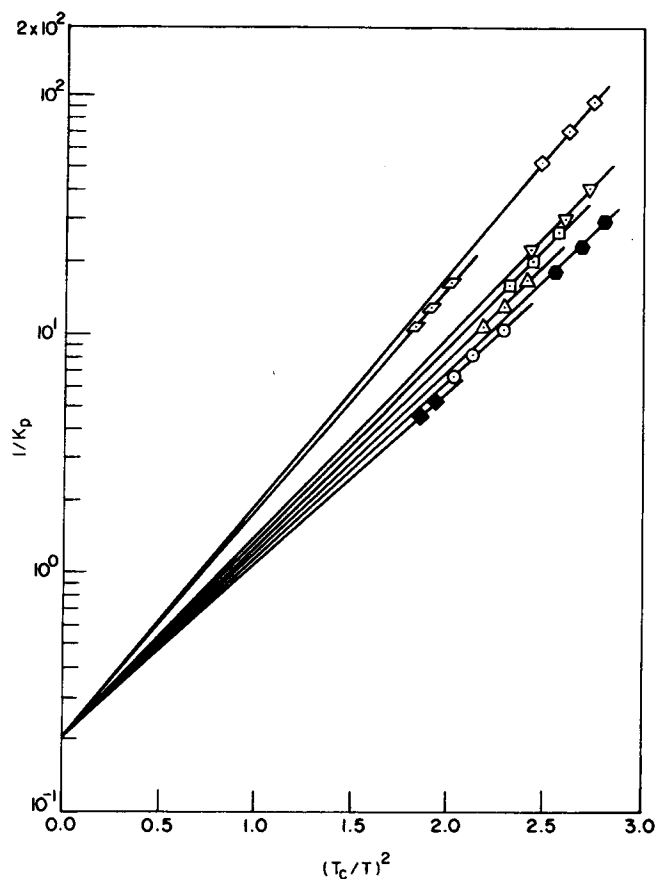


Fig. 8. $\ln(1/K_p)$ versus $(T_c/T)^2$ for nonpolar and slightly polar solutes in PVAc. \circ *n*-nonane; \triangle *n*-decane; \square *n*-undecane; ∇ *n*-dodecane; \blacklozenge cyclohexane; \bullet *n*-butylcyclohexane; \square benzene; \diamond *n*-butylbenzene. (Data taken from Ref. 11)

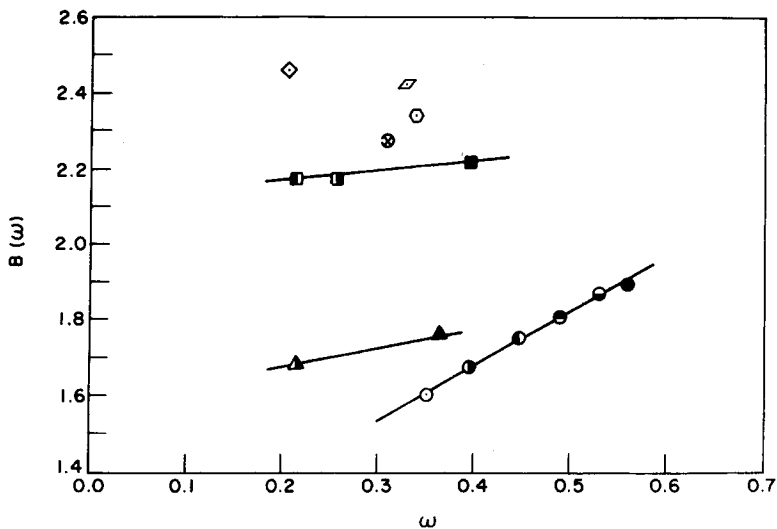


Fig. 9. Slope B versus acentric factor ω for organic solutes in PVAc. \circ *n*-heptane; \bullet *n*-octane; \bullet *n*-nonane; \bullet *n*-decane; \bullet *n*-undecane; \bullet *n*-dodecane; \blacktriangle *n*-butylcyclohexane; \blacktriangle cyclohexane; ∇ carbon tetrachloride; \diamond chloroform; \square benzene; \blacksquare toluene; \blacksquare *n*-butylbenzene; \otimes acetone; \square methyl ethyl ketone; \odot vinyl acetate.

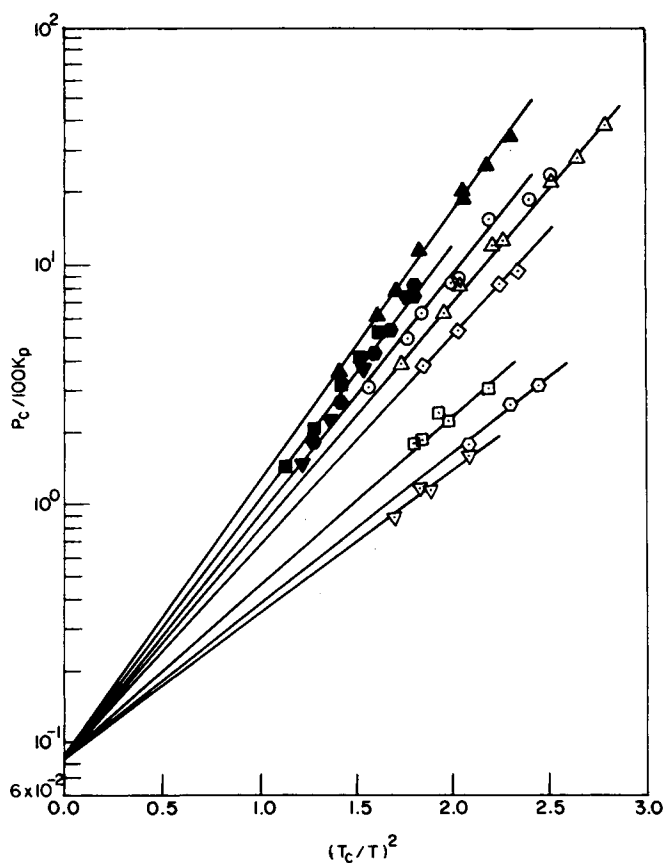


Fig. 10. $\ln(P_c/100K_p)$ versus $(T_c/T)^2$ for organic solutes in PVAc. Symbols are the same as in Figure 7.

TABLE IV
Average Error Between Experimental and Calculated Values of $P_c/100K_p$ for Poly(vinyl Acetate)

Solute	No. points	T ($^{\circ}\text{C}$)	Slope B^a	ω	Average % error	References
<i>n</i> -Octane	3	90–120	1.519	0.394	4.23	8
<i>n</i> -Heptane	4	100–140	1.448	0.351	3.73	7, 8
Toluene	9	80–200	2.254	0.257	3.73	6, 7, 8
Benzene	9	80–200	2.330	0.212	5.89	6, 7, 8
Cyclohexane	4	100–140	1.742	0.213	7.59	7, 8
Carbon tetrachloride	4	90–135	2.096	0.194	5.12	8, 10
Chloroform	8	80–175	2.680	0.216	3.97	6, 8, 10
Vinyl acetate	4	125–200	2.486	0.340	5.72	9
Methyl ethyl ketone	6	125–200	2.356	0.329	5.24	7, 9
Acetone	6	125–200	2.432	0.309	3.12	7, 9

^aWith a common intercept, $A = -2.579$ in eq. (4).

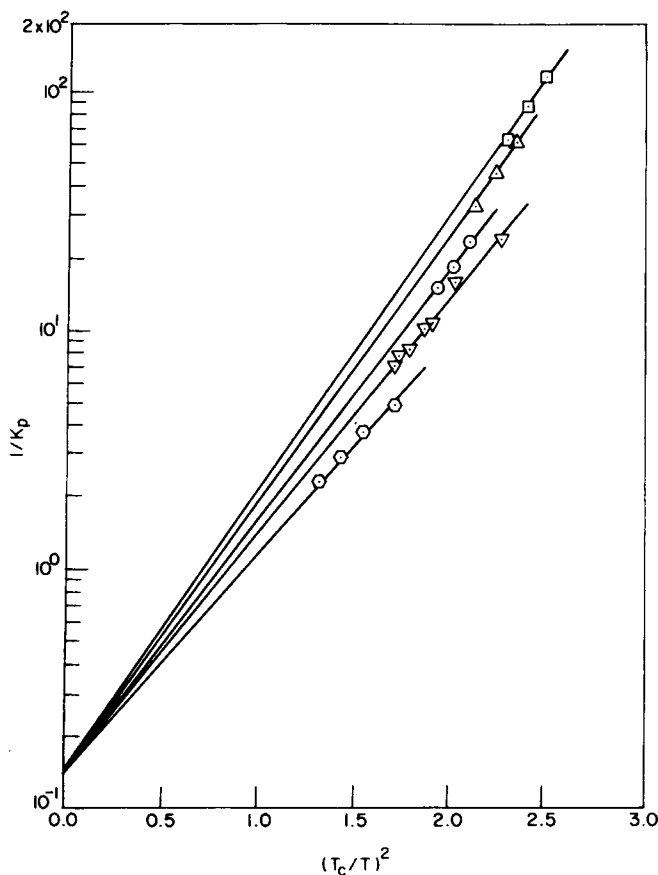


Fig. 11. $\ln(1/K_p)$ versus $(T_c/T)^2$ for *n*-alkanes in PS. \odot *n*-heptane; ∇ *n*-decane; \odot *n*-dodecane; Δ *n*-tetradecane; \square *n*-hexadecane. (Data taken from Ref. 13.)

Correlation of the Solubility of Organic Solutes in Polystyrene

In order to minimize any possible confusion that may arise from plotting all the data on a single sheet, we have plotted the solubility data of 17 solutes covering 82 data points for PS in three separate sheets, as given in Figures 11 through 13. Note that Figure 11 contains the solubility data for five nonpolar *n*-alkanes (*n*-heptane, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane), Figure 12, contains the solubility data for five slightly polar aromatic solutes (*n*-butylbenzene, ethylbenzene, chlorobenzene, toluene, and benzene) and two aliphatic cyclic compounds (cyclohexane and *n*-butylcyclohexane), and Figure 13 contains the solubility data for five strongly polar solutes (cyclohexanone, methyl ethyl ketone, acetonitrile, dioxane, and 1,2-dichloroethane). The procedure employed for drawing least-squares lines through the data points in Figures 11 through 13 is the same as that described in reference to Figure 7. That is, in these figures we have used a common intercept, -2.028 , which is the average value of the intercepts for the 17 solutes considered.

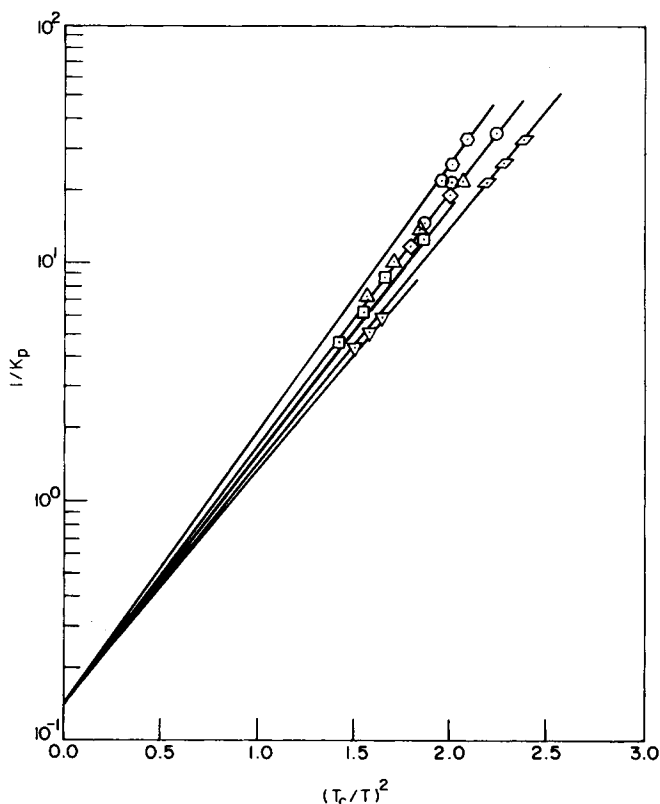


Fig. 12. $\ln(1/K_p)$ versus $(T_c/T)^2$ for nonpolar and slightly polar solutes in PS. \odot ethylbenzene^{12,14}; \triangle toluene^{12,14}; \square benzene¹²⁻¹⁴; \diamond chlorobenzene¹⁴; \circ *n*-butylbenzene¹³; \square *n*-butylcyclohexane¹³; ∇ cyclohexane.¹²⁻¹⁴

It is seen in Figures 11 through 13 that the slope of the $\ln(1/K_p)$ versus $(T_c/T)^2$ plots varies with the type of solute, very similar to the situations considered for the solubility in PVAc (see Figures 7 and 8). In order to facilitate our discussion, in Table III we have given values of slope B determined by least-squares analysis using eq. (1), the acentric factor ω of the solutes, and the average percentage of error for the 17 solutes considered in PS.

Figure 14 gives plots of B versus ω for the 17 organic solutes. The following observations may be made on the correlation displayed in Figure 14 (for comparison purposes, see also Figure 9). (1) Values of B for the five nonpolar *n*-alkanes increase linearly with ω . This relationship is very similar to that observed with PVAc. (2) For cyclohexane and *n*-butylcyclohexane in PS, the dependence of B on ω is very similar to that observed with PVAc. (3) Values of B for the five slightly polar organic aromatic solutes increase linearly with ω , very similar to that observed with PVAc. (4) For the five strongly polar solutes, no clear relationship between B and ω can be established. It is of great interest to note in Figure 14 that, at the same value of ω , values of B for the strongly polar solutes are smaller than those for the slightly polar solutes, which is in contrast to the situation observed with PVAc.

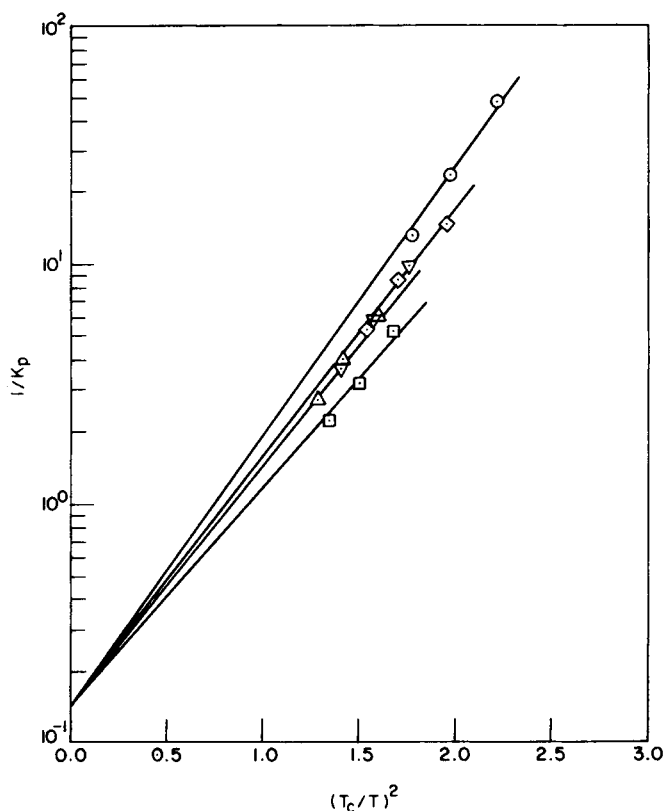


Fig. 13. $\ln(1/K_p)$ versus $(T_c/T)^2$ for strongly polar solutes in PS. \odot cyclohexanone¹⁴; Δ methyl ethyl ketone¹⁴; \square acetonitrile¹⁴; ∇ 1,2-dichloroethane¹⁴; \diamond dioxane^{12,14}.

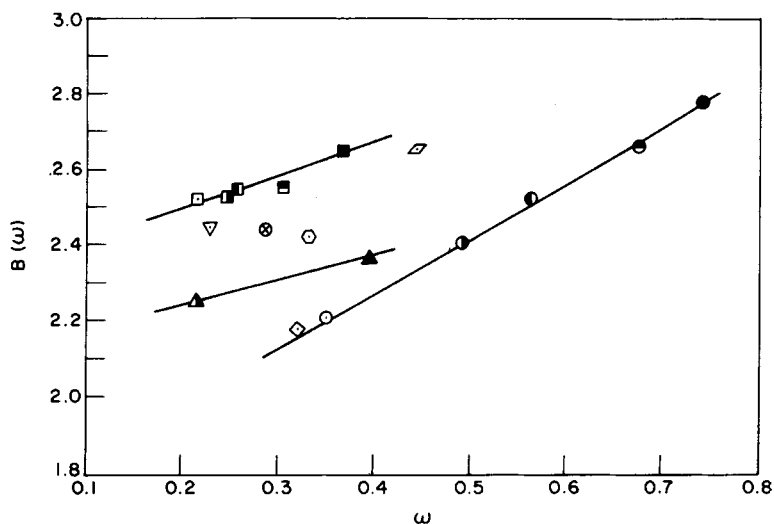


Fig. 14. Slope B versus acentric factor ω for organic solutes in PS. \bullet *n*-hexadecane; \ominus *n*-tetradecane; \odot *n*-dodecane; \bullet *n*-decane; \circ *n*-heptane; \blacktriangle *n*-butylcyclohexane; \triangle *n*-cyclohexane; \square benzene; \blacksquare chlorobenzene; \blacksquare toluene; \square ethylbenzene; \blacksquare *n*-butylbenzene; \square cyclohexanone; \otimes 1,2-dichloroethane; ∇ dioxane; \odot methyl ethyl ketone; \diamond acetone.

At this juncture, it is appropriate to mention that the correlations presented in Figures 11 through 13 are at variance with those reported earlier by Stiel and Harnish,¹ in that, using 109 data points for several solutes, they obtained a *single* least-squares line. It should be pointed out, however, that in their correlation, Stiel and Harnish included the solubility data for various gases (e.g., methane, carbon dioxide, and propane) and polar solutes (e.g., methyl ethyl ketone, chloroform, 1,2-dichloroethane, chlorobenzene, methyl chloride, and methylene chloride). Moreover, they utilized solubility data obtained from various sources, including data obtained by the high-pressure sorption method and also by the quartz spring sorption method. Note that, in general, sorption methods generate solubility data at finite concentrations, and therefore one must extrapolate the data to infinite dilution in order to utilize them in the Henry's law region. In general, extrapolation introduces errors whose magnitude is difficult to estimate.

In this investigation, we have used solubility data from three different sources,¹²⁻¹⁴ all of which employed gas-liquid chromatography and presented the data in terms of the specific retention volume, weight-fraction Henry's constant, or activity coefficient at infinite dilution. Since such data were obtained in the Henry's law region, no extrapolation was necessary for us to obtain the correlations presented in Figures 11 through 13. As a matter of fact, the data of Newman and Prausnitz¹⁴ that were used in Figures 11 through 13 had also been used in the correlation by Stiel and Harnish.¹ However, the data of Galin and Rupprecht¹² and DiPaola-Baranyi and Guillet,¹³ which were published in 1978, were not available at the time when Stiel and Harnish prepared their manuscript.

CONCLUDING REMARKS

We have attempted to obtain correlations on the solubility of organic solutes at infinite dilution in PVAc and PS at elevated temperatures, utilizing literature data that include 16 solutes covering 81 data points for PVAc and 17 solutes covering 82 data points for PS. It has been found that, in both PVAc and PS, plots of $\ln(1/K_p)$ versus $(T_c/T)^2$ give rise to a linear relationship represented by eq. (1). We have found that the slope B of such plots varies with the acentric factor ω , but no definite correlation between B and ω could be established for all the solutes considered. A comparison of Tables I and II with Table III reveals, however, that the dependence of the slope B on ω is weak for PS, compared with that for PVAc.

However, the present investigation has revealed differences in solubility behavior between nonpolar and polar solutes in PVAc, and PS, respectively. Specifically, we have found that (1) in both PVAc and PS, at the same value of ω , values of B are larger for slightly polar aromatic solutes than for nonpolar solutes; and (2) at the same value of ω , values of B for PS are smaller for strongly polar solutes than for slightly polar solutes, whereas the opposite trend is found for PVAc. This observation may be interpreted as meaning that the solubility of strongly polar solutes is greater in PVAc than in PS.

Therefore, it can be concluded from the present investigation that the polarities of both solutes and polymers have a strong influence on the

solubility of organic solutes in a polymer at elevated temperatures. More research effort is needed to establish quantitative relationships between the polarity and other structural parameters of solutes and structural parameters of polymers in order to predict the solubility of organic solutes in polymers at elevated temperatures.

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