Application of Gas–Liquid Chromatography to the Thermodynamics of Polymer Solutions

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Received June 11, 1970

It has been well established[3–7] that gas–liquid chromatography (glc) can give accurate thermodynamic data on binary solutions where the components differ considerably in volatility or molecular weight. The substance of lower molecular weight (component 1) is injected into the moving gas phase and dissolves at effectively infinite dilution in the stationary liquid phase. This is formed by the higher molecular weight material, for example,[3] squalane, biphenyl, dinonyl phthalate, glycerol, or the higher *n*-alkanes such as C_{16}, C_{24}, C_{36}, etc. The convenience of the technique is such that activity coefficient data have already been obtained for hundreds of systems. In contrast, activity data are available for far fewer high polymer systems, in part certainly because of the need to use the laborious vapor sorption technique. While that technique gives activity data as a function of concentration, it would still be desirable to have data at infinite dilution for a variety of systems in order to test contemporary theories of polymer solution thermodynamics.[8,9]

Recently Guillet[10] and coworkers have applied the glc technique to systems in which the stationary phase is a high polymer.[11] Their primary interest has been to demonstrate the versatility of the technique in determining first- and second-order phase transitions, degrees of crystallinity, and other physical characteristics of the polymer, while the present communication considers the determination of thermodynamic quantities. It has been prompted by comments from several workers who have noted the difficulty of applying the usual thermodynamic equations of glc which yield γ_1^∞, the activity coefficient of component 1 at infinite dilution (eq 5 and 6). The equations require an *exact* value of the molecular weight of component 2, making difficult their use for polymer systems. Our main objective is to resolve this problem. However, we also wish to stress the utility of the technique in providing data with which to test contemporary theories of polymer solution thermodynamics. We therefore comment on equations which directly relate experimental glc data to the interaction parameter, χ, of polymer solution thermodynamics.

The Thermodynamic Equations of Glc. The primary glc data are the retention time, *i.e.*, the time taken by component 1 to traverse the column, and the retention volume, V_R, the volume of carrier gas passing through during that time. The net retention volume is defined as $V_N = V_R - V_{\text{gas}}$, where V_{gas} is the volume of gas in the column (gas hold-up). For thermodynamic applications[3,6a] this quantity is obtained at, or extrapolated to, negligible or zero column pressure, giving V_N^0. The partition coefficient, k_0, is defined by

$$k_0 = (N_{1,\text{liq}}/V_{\text{liq}})/(N_{1,\text{gas}}/V_{\text{gas}}) \tag{1}$$

and is simply determined from glc through

$$k_0 = V_N^0/V_{\text{liq}} \tag{2}$$

Here the N_1 are numbers of moles in the liquid and gas phases. Since k_0 characterizes the partitioning of component 1 between gas and liquid phases, it decreases rapidly with increasing temperature. At an early point in the development of glc, it seemed advisable to convert k_0 to a quantity considered characteristic of the interaction between the two components in the liquid phase. Following Porter, Deal, and Stross,[12] the chosen quantity has been the rational activity coefficient, γ_1, of component 1. This is defined as the ratio of two quantities: (1) the activity, a_1, *i.e.*, the ratio of the fugacity f_1 to the fugacity, f_1^0, in the standard state, pure liquid 1, and (2) a reference function chosen to be the mole fraction, x_1. Thus

$$\gamma_1 \equiv a_1/x_1 \equiv f_1/x_1f_1^0 \tag{3}$$

If the gas were ideal, *i.e.*, $f_1 = P_1$ and $f_1^0 = P_1^0$, eq 1–3 give for γ_1 as $x_1 \to 0$

$$\gamma_1^\infty = RTN_{2,\text{liq}}/P_1^0V_N^0 \tag{4}$$

where $N_{2,\text{liq}}$ is the number of moles of component 2 in the liquid phase. Correcting[3] for the effect of finite pressure P_1^0 on the chemical potential of component 1 in gas and liquid states, eq 4 becomes

$$\ln \gamma_1^\infty = \ln\left[\frac{RTN_{2,\text{liq}}}{P_1^0V_N^0}\right] - \frac{P_1^0}{RT}(B_{11} - V_1) \tag{5}$$

Here B_{11} is the gas-state second virial coefficient of component 1 and V_1 is the liquid-state molar volume. Many authors[3] have used the specific retention volume, V_g^0 equal to V_N^0 per gram of liquid phase, and converted to 0°, using the ideal gas equation. Equation 5 becomes

$$\ln \gamma_1^\infty = \ln\left[\frac{(273.2)R}{P_1^0V_g^0M_2}\right] - \frac{P_1^0}{RT}(B_{11} - V_1) \tag{6}$$

with M_2 the molecular weight of component 2.

Circumvention of the Polymer Molecular Weight in the Glc Equations. Equation 5 or 6 raises a difficulty in the apparent need of defining M_2 for a polymer; this quantity may be the more difficult to specify in the case of polydispersity. Furthermore, it is unacceptable intuitively that $\ln \gamma_1^\infty$ should depend increasingly critically on the polymer molecular weight as $M_2 \to \infty$ tending, in the limit, to $\ln \gamma_1^\infty = -\infty$. This difficulty is inescapable when component 2 is a high polymer. However, it suggests that the rational activity coefficient may

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(3) C. L. Young, *Chromatogr. Rev.*, **10**, 129 (1968).

(4) D. H. Everett and C. T. Stoddard, *Trans. Faraday Soc.*, **57**, 746 (1961).

(5) (a) D. E. Martire in "Gas Chromatography," L. Fowler, Ed., Academic Press, New York, N. Y., 1963, p 33; (b) D. E. Martire and L. Z. Pollara in "Advances in Chromatography," Vol. I, J. C. Gidding and R. A. Kellerd, Ed., Marcel Dekker, New York, N. Y., 1966, p 335.

(6) (a) A. J. B. Cruickshank, M. L. Windsor, and C. L. Young, *Proc. Roy. Soc., Ser. A*, **295**, 259, 271 (1966); (b) A. J. B. Cruickshank, B. W. Gainey, and C. L. Young, *Trans. Faraday Soc.*, **64**, 337 (1968).

(7) J. R. Conder in "Progess in Gas Chromatography," J. H. Purnell, Ed., Wiley, New York, N. Y., 1968, p 209.

(8) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035 (1968).

(9) D. Patterson, *J. Polym. Sci., Part C*, No. 16, 3379 (1968).

(10) (a) O. Smidrød and J. E. Guillet, *Macromolecules*, **2**, 272 (1969); (b) A. Lavoie and J. E. Guillet, *ibid.*, **2**, 443 (1969); (c) J. E. Guillet and A. N. Stein, *ibid.*, **3**, 102 (1970).

(11) J. E. Guillet, *et al.*, refer to the gas-phase component as the molecular "probe." This avoids the glc terminology in which that component is the solute and the stationary-phase polymer would be the solvent. This terminology is confusing to polymer chemists used to solutions where the polymer is the solute, being present at low, rather than high, concentrations.

(12) P. E. Porter, C. H. Deal, and F. H. Stross, *J. Amer. Chem. Soc.*, **78**, 2999 (1956).

TABLE I
CALCULATED ACTIVITY COEFFICIENTS FOR *n*-HEXANE AT INFINITE DILUTION IN *n*-ALKANES

n-Alkane	Ln γ_1^∞	Ln $(a_1/w_1)^\infty$
C_{20}	−0.10	0.90
C_{40}	−0.39	1.25
C_{60}	−0.65	1.39
C_{100}	−1.03	1.50
C_{1000}	−3.14	1.67
C_∞	$-\infty$	1.69

not be the most meaningful quantity to report in ordinary glc work, where M_2, although necessarily large, is still determinable exactly. The choice of the mole fraction, x_1, as the reference function with which to compare a_1 in eq 3 is convenient when dealing with a mixture of equal-sized molecules, *i.e.*, a regular solution. There the quantity γ_1^∞ is characteristic of the interaction between the two components, but this is no longer the case with a mixture of molecules of different size, and *a fortiori*, for polymer solutions. Mathematically, x_1 becomes a most inconvenient composition variable in eq 3, reminding us that the ideal solution concept and indeed the concepts of rational activity coefficients and excess thermodynamic quantities are of little use in polymer solution thermodynamics. As an illustration, Table I shows calculated values of ln γ_1^∞ for *n*-hexane at 35° in a series of *n*-alkanes of increasing carbon number. (The values were obtained using the theoretical correlation of Cruickshank, Gainey, and Young,[6b] *i.e.*, their eq 20 and 7, with $w/kT = 0.471$.) Instead of approaching an asymptotic limit, ln γ_1^∞ varies rapidly, showing that it is not characteristic of the interaction of *n*-hexane with its *n*-alkane surroundings. A more suitable reference function than x_1 could be any concentration variable for component 1 which does not involve the number of moles of component 2, *e.g.*, weight fraction, volume fraction, molality, molarity, etc.[13] Choosing weight fraction, w_1, eq 6 is changed to

$$\ln\left(\frac{a_1}{w_1}\right)^\infty = \ln\left[\frac{273.2R}{P_1^0 V_g^0 M_1}\right] - \frac{P_1^0}{RT}(B_{11} - V_1) \qquad (7)$$

where M_1 is the molecular weight of component 1. The relationship between $(a_1/w_1)^\infty$ and the experimental V_g^0 is now unambiguous and does not require specific experimental knowledge of M_2 or of the polydispersity. (Of course a_1/w_1 still depends on these factors, but through the *observed* retention volume, V_g^0.) Table I also shows ln (a_1/w_1), which tends to an asymptotic limit with increasing carbon number of component 2, as required of any parameter characteristic of 1–2 interactions.[14]

Application of Statistical Thermodynamic Theories to the Glc Case. The development of eq 7 indicates that glc experiments may be useful in providing a rapid, readily applicable route to the evaluation of thermodynamics of polymer solutions. The technique may be particularly valuable for the determination of χ parameters discussed in recent solution theories.[8,9] The glc route would yield χ only at infinite dilution of component 1, but would do so rapidly and therefore permit a critical test to be made of various theoretical predictions of this parameter. An equation linking glc quantities with χ is therefore desirable.

Statistical theories of solution thermodynamics express the activity of a component as the sum of two contributions: (i) a combinatorial (or athermal, or configurational) entropy and (ii) a noncombinatorial (or thermal, or interactional) free energy of mixing. The latter contribution is characteristic of the 1–2 interaction and its determination is the goal of activity measurements on polymer solutions. The value of the combinatorial entropy is calculated from a theory, but in a completely unambiguous way. When the familiar Flory–Huggins theory is used, we have

$$\begin{aligned}\ln a_1 &= (\ln a_1)_{\text{comb.}} + (\ln a_1)_{\text{noncomb.}} \\ &= \left[\ln \phi_1 + \left(1 - \frac{1}{r}\right)\phi_2\right] + \chi\phi_2^2\end{aligned} \qquad (8)$$

Here χ is obtained by dividing $(\ln a_1)_{\text{noncomb.}}$ by ϕ_2^2. Thus it may always be obtained from experiment, but its significance as a parameter characterizing polymer–solvent interaction depends on the validity of the Flory–Huggins expression. In eq 8, the volume fraction is given by

$$\phi_1 = \frac{w_1 v_1}{w_1 v_1 + w_2 v_2} \qquad (9)$$

where v_1 and v_2 are the specific volumes of the low molecular weight substance and the polymer, respectively. For polydisperse solvents, r is given by the equation

$$r = (\bar{V}_2)_n/V_1 = (\bar{M}_2)_n v_2/V_1 \qquad (10)$$

where $(\bar{V}_2)_n$ is the number-average of the molar volumes in the polydisperse polymer sample, V_1 is the molar volume of the (monodisperse) component 1, and v_2 is the specific volume of the polymer. One might calculate v_2 from published $v(M)$ data for sharp fractions. Since v is usually of the form $v(M) = v(\infty) - \text{constant}/M$, the specific volume of the polydisperse sample should be approximately equal to that of a sharp fraction having $M = \bar{M}_n$. It is clear that eq 8 will not depend critically on v_2.

We remark that both terms of $(\ln a_1)_{\text{comb.}}$ in eq 8 must be temperature dependent. This point is considered in more detail in an Appendix which deals with the temperature dependence of ln a_1 more generally.

For the limiting case in which $\phi_2 \to 1$, eq 8 becomes

$$\ln\left(\frac{a_1}{w_1}\right)^\infty = \ln\frac{v_1}{v_2} + \left(1 - \frac{V_1}{\bar{M}_2 v_2}\right) + \chi \qquad (11)$$

and from eq 7

$$\chi = \ln\left[\frac{273.2Rv_2}{P_1^0 V_g^0 V_1}\right] - \left(1 - \frac{V_1}{\bar{M}_2 v_2}\right) - \frac{P_1^0}{RT}(B_{11} - V_1) \qquad (12)$$

Equation 12 represents the sought-for link between the experimental glc datum (V_g^0) and the thermodynamic interaction parameter, as defined by the traditional Flory–Huggins approach to solution thermodynamics.

There is now both theoretical and experimental justification[8,9] for regarding χ in eq 8 as being concentration dependent—*i.e.*, adding additional terms in higher powers of ϕ_2. In view of this, two points are stressed: (1) the value of χ at infinite dilution obtained by glc will in general differ from that obtained at other concentrations by conventional methods, and (2) the glc value of χ in eq 11 and 12 is in fact

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(13) See F. T. Wall "Chemical Thermodynamics," W. H. Freeman, San Francisco, Calif., 1958, p 343, for a discussion of generalized activity coefficients.

(14) We note that a point similar to the above has been made in a recent discussion [I. D. Kuntz, F. P. Gasparro, M. D. Johnston, and R. P. Taylor, *J. Amer. Chem Soc.*, 90, 4778 (1968)] of the use of equilibrium constants K_x and K_c in reporting equilibria of reactions in solution. The constant K_x is sensitive to the molecular weight of the solvent in the same way as γ_1 in glc, and K_c is therefore the preferred constant to report.

TABLE II
INTERACTION PARAMETERS FOR ALKANE + POLYETHYLENE SYSTEMS

System	Range, °C	Ln $(a_1/w_1)^\infty$	χ (eq 8)	χ^* (eq 9)
n-Dodecane + B-PE	110–145	1.35	0.18 ± 0.01^a	0.27 ± 0.01^a
n-Decane + L-PE	145–190	1.41	0.18 ± 0.005^a	0.32 ± 0.005^a

[a] Standard deviation, giving precision of result defined by V_g^0 reproducibility. However, due to limitations in definition of weight of stationary phase, accuracy of present χ (χ^*) is ±0.05.

the whole noncombinatorial contribution to ln a_1 at infinite dilution, and is independent of any assumed theoretical form of $(\ln a_1)_{\text{noncomb.}}$ However, the value of $(\ln a_1)_{\text{noncomb.}}$ does depend on the estimate of the combinatorial contribution to ln a_1. This is readily indicated by adopting the recent suggestion of Flory and collaborators who replace volume fraction in eq 9 with segment fraction and specific volumes with specific "core" volumes. The new volumes (v^*) are also referred to as reduction parameters and correspond to the close-packed specific volumes of the hypothetical liquids at 0°K. In view of these changes, r is redefined in terms of eq 10, but with starred volumes. It is clear that the combinatorial entropy is now independent of temperature. The result of interest then is the resulting change in eq 12 which now becomes

$$\chi^* = \ln\left[\frac{273.2Rv_2^*}{P_1^0V_g^0V_1^*}\right] - \left(1 - \frac{V_1^*}{\bar{M}_2v_2^*}\right) - \frac{P_1^0}{RT}(B_{11} - V_1) \quad (13)$$

To help differentiate between χ as determined by eq 12 and 13 we use a star superscript, although this is not done in the Flory nomenclature.[8]

In our view, it is not clear which of the two estimates of the combinatorial entropy is the more accurate. Accordingly, in illustrating the use of glc data in evaluations of χ, we have used both eq 12 and 13 with data for the systems *n*-dodecane + (low density) polyethylene and *n*-decane + (linear) polyethylene. These χ and χ^* values, listed in Table II, are average quantities for the temperature range 100–145° for the branched polymer and 140–190° for the linear polyethylene system. They utilize the V_g^0 data of Guillet and Stein[10c] for the former system, as yet unpublished V_g^0 data of Gray and Guillet for the latter system, and volume data for both components determined by Orwoll and Flory.[15] The tabulation shows the sensitivity of the parameters to whether starred or unstarred volume quantities are used. The source of this sensitivity is the logarithmic term in eq 12 and 13.

It is noteworthy that the values calculated from eq 13 are highly consistent with χ values obtained from literature glc data for alkane systems in which the stationary phase is not a high polymer. In a forthcoming publication[16] we will further discuss this matter as well as the application of newer theories of polymer solution thermodynamics to a variety of alkane systems.

The role of B_{11} in determining values of thermodynamic quantities can be very important. This correction for gas-phase imperfections makes only a relatively small difference in the calculations of χ, but the same is not true when such thermodynamic data as enthalpies are to be calculated from the temperature dependence of V_g^0. From eq 7, the partial molar heat of the solute at infinite dilution in the polymer ($\bar{h}_1$), relative to that in the pure liquid state, h_1^0, is given by

$$\begin{aligned}\Delta\bar{h}_1^\infty &= \bar{h}_1^\infty - h_1^0 = R\partial \ln a_1/\partial(1/T) \\ &= R\frac{\partial}{\partial(1/T)}\left[-\ln V_g^0P_1^0 - \frac{P_1^0}{RT}(B_{11} - V_1)\right]\end{aligned} \quad (14)$$

The significance of $\Delta\bar{h}_1^\infty$ and its relation to $\partial\chi/\partial T$ are discussed further in the Appendix.

We have examined the data of Guillet and Stein[10c] and as yet unpublished results for *n*-decane + polyethylene in terms of eq 14. The examination discloses that the partial derivative with respect to $1/T$ of the logarithmic term is essentially zero, the sign and absolute value of the calculated $\Delta\bar{h}_1^\infty$ being determined largely by the reciprocal temperature derivative of the correction term containing the B_{11} coefficient. Accurate values of B_{11} and the inclusion of the correction term in eq 14 are prerequisites, therefore, for meaningful evaluation of such thermodynamic parameters as $\Delta\bar{h}_1^\infty$.

Acknowledgment. We wish to thank Dr. J. Biroš, Institute of Macromolecular Chemistry, Prague, and Dr. G. C. B. Cave of this department for most stimulating discussions of the subject material. We express our appreciation to the National Research Council of Canada for financial support.

Appendix

The Flory–Huggins Combinatorial Entropy and the Temperature–Volume Fractions. The Flory–Huggins approximation for the combinatorial entropy of mixing is

$$(\Delta S_m)_{\text{comb.}} = -k[N_1 \ln \phi_1 + N_2 \ln \phi_2] \quad (15)$$

It is used frequently as in the present work as a contribution to the free energy of mixing

$$(\Delta G_m)_{\text{comb.}} = kT[N_1 \ln \phi_1 + N_2 \ln \phi_2] \quad (16)$$

The above expressions were developed on the assumption of a rigid-lattice model, justifying the neglect of temperature variations in ϕ. In practice, however, the volume fractions do vary with temperature, a fact which is especially important in polymer solutions because of the sizable difference in thermal expansion coefficients of the polymer and low molecular weight components. Equations 15 and 16 are therefore inconsistent, since $(\partial\Delta G_m/\partial T)_p \neq -\Delta S_m$. If one of the pair of equations is assumed correct, then the other must be revised by the addition of a term accounting for the temperature dependence of ϕ.

It is noted that the Flory–Huggins result can be obtained without recourse to a lattice model. The approach of Longuet-Higgins[17] is a well-known example of this. In his work, eq 16 is obtained, (15) being arrived at by differentiation, keeping ϕ constant. This procedure appears at first hand to involve the above inconsistency; however, in obtaining the result, Longuet-Higgins introduced an assumption which is similar to that of a rigid lattice, *viz.*, that the components have the same "density" as the solution, *i.e.*, the same degree of thermal expansion. It is evident, therefore, that the "volume fractions" of Longuet-Higgins[17] are effectively segment fractions and hence independent of temperature. There is, therefore, no serious inconsistency in the earlier work.

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(15) R. A. Orwoll and P. J. Flory, *J. Amer. Chem. Soc.*, **89**, 6814 (1967).

(16) Y. B. Tewari, D. Patterson, and H. P. Schreiber, to be published.

(17) H. C. Longuet-Higgins, *Discuss. Faraday Soc.*, **15**, 73 (1953).

A further consequence of a temperature dependent ϕ is expressed by $\partial(\Delta G_m/T)/\partial T \neq 0$. As a consequence, a combinatorial contribution to ΔH_m must be recognized, as has been done already by Everett and Munn[18] for the system *n*-hexane + *n*-hexadecane. They obtain this contribution by assuming eq 16 to be the correct expression for (ΔG_m). Another possibility would be to accept eq 15, and use a revised version of (16) to obtain (ΔH_m). In our work, eq 11 corresponds to (16), whence

$$\begin{aligned}\Delta \bar{h}_1^{\infty} &= R\frac{\partial \ln a_1}{\partial(1/T)} = R\frac{\partial}{\partial(1/T)}[\ln v_1/v_2 + \chi] \\ &= RT^2(\alpha_2 - \alpha_1) + R[\partial\chi/\partial(1/T)]\end{aligned} \tag{17}$$

Here α_1 and α_2 are thermal expansion coefficients for the components of the liquid state. Typically, $\alpha_1 \sim 10^{-3}$, $\alpha_2 \sim 5 \times 10^{-4}$ deg^{-1}, $T = 300$°K, making the combinatorial contribution to $\Delta \bar{h}_1^{\infty}$ of the order of −100 cal. Values of $\Delta \bar{h}_1^{\infty}$ extrapolated from calorimetric heats of dilution to high concentrations of polymer tend to fall in the range 0–400 cal. (For example, a very large value of $\Delta \bar{h}_1^{\infty} \simeq 360$ cal has been obtained for the system polyisobutylene–benzene.[19]) The importance of the combinatorial contribution is evident. On the other hand, using segment fractions in the combinatorial entropy (*e.g.*, our eq 13) produces simply

$$\Delta \bar{h}_1^{\infty} = R[\partial\chi^*/\partial(1/T)] \tag{18}$$

Recent statistical theories[8] attempt to predict the χ parameter and its temperature dependence using only data on the pure components. The theories should be capable of deciding which of the expressions for the combinatorial entropy produces more consistent values of χ (or χ^*) and the respective temperature dependences. Since the combinatorial contribution to $\Delta \bar{h}_1^{\infty}$ is completely formal, we would expect the segment fraction route, leading to χ^*, to be superior.

[18] D. H. Everett and R. J. Munn, *Trans. Faraday Soc.*, **60**, 1951 (1964).

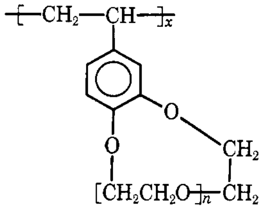
[19] M. A. Kabayama and H. Daoust, *J. Polym. Sci., Part C*, **No. 62**, 1127 (1958).

Communications to the Editor

Cation Binding Properties of Poly(vinyl macrocyclic polyethers)

Considerable interest is currently shown in the cation binding properties of macrocyclic polyethers, a class of compounds recently synthesized and studied by Pedersen.[1] The so-called crown compounds strongly increase the solubility of inorganic salts in nonpolar media[1] and form crystalline complexes with many salts.[2,3] They are found to affect greatly the ion pair structure of alkali carbanion salts[4] and the reaction rate and stereospecific course of reactions involving ion pairs.[5] The cyclic polyethers have also gained prominence as model compounds for the study of ion movement across biological membranes. Eisenman, *et al.*,[6] and others[7,8] have found that the specific effect exerted by these crown compounds on the cation transport resembles that of natural ion carriers such as monactin and valinomycin.

We would like to report some interesting results on the cation binding properties of polymers containing the macrocyclic polyether moiety as a pendant group. We were particularly interested in comparing the properties of these polymers with those of the monomeric analogs in order to determine the extent of cooperative effects in the cation complexation of the polymeric species. Two polymers were investigated, *i.e.*, poly(2,3-4′-vinylbenzo-1,4,7,10,13-pentaoxacyclopentadec-2-ene) or poly(vinylbenzo-15-crown-5) (P-15C5) and poly(2,3-4′-vinylbenzo-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene) or poly(vinylbenzo-18-crown-6) (P-18C6). They can be prepared from the corresponding vinyl monomers by a radical initiator, or anionically with sodium α-methylstyrene tetramer in THF at −80°. Molecular weights of 100,000 are easily obtainable. The structures of the repeating units are depicted below.



P-15C5, $n = 3$
P-18C6, $n = 4$

The actual complexation behavior was investigated by a method similar to one employed by Pedersen[9] and others.[10] Picric acid is dissolved in aqueous hydroxide containing the desired cation and the solution shaken with an equal quantity of an immiscible organic solvent (*e.g.*, methylene chloride) containing the poly(vinyl crown) compound or its monomeric analog (the latter one contains a methyl group at the 4′ position, the two compounds being denoted as 15C5 and 18C6). After equilibrium is reached, the picrate salt concentration in the organic layer is measured by optical spectroscopy.

The results, presented in Table I, are expressed as per cent of picrate salt extracted, based on the total amount of picrate present. While the picrate transfer depends on the complexing strength of both the water and cyclic polyether, as well as on the partition coefficients of the various species,[10] the extracted amount of picrate nevertheless is indicative of the cation complexing efficiency of the respective crown species.

Focusing only on the different behavior of polymer and "monomer," one observes a strong increase in the complexing efficiency of P-15C5 as compared to 15C5, especially for the

[1] C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); **92**, 391 (1970).

[2] C. J. Pedersen, *ibid.*, **92**, 386 (1970).

[3] D. Bright and M. R. Truter, *J. Chem. Soc. B*, 1544 (1970).

[4] K. H. Wong, G. Konizer, and J. Smid, *J. Amer. Chem. Soc.*, **92**, 666 (1970).

[5] J. Almy, D. C. Garwood, and D. J. Cram, *ibid.*, **92**, 4321 (1970).

[6] G. Eisenman, S. M. Ciani, and G. Szabo, *Fed. Proc., Fed. Amer. Soc. Exp. Biol.* **27**, 1289 (1968).

[7] H. Lardy, *ibid.*, **27**, 1278 (1968).

[8] D. C. Tosteson, *ibid.*, **27**, 1269 (1968).

[9] C. J. Pedersen, *ibid.*, **27**, 1305 (1968).

[10] G. Eisenman, S. Ciani, and G. Szabo, *J. Membrane Biol.*, **1**, 294 (1969).