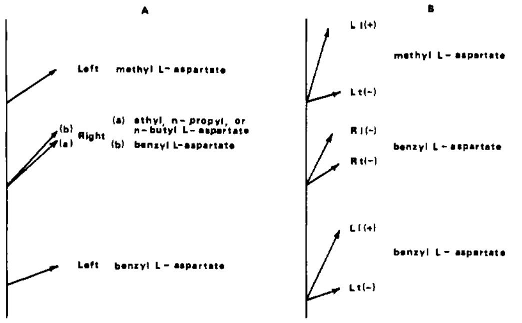

Figure 4. Direction of –C–O–C– line for poly(aspartate esters) (A) from solid films and (B) for isolated polymer chains (calculated).

dict as having a longitudinal orientation. This polymer, however, was also calculated to have a left-handed helix sense and not the observed right-handed sense. In the series of poly(alkyl aspartate esters), the helix sense is calculated to be left-handed for the methyl and ethyl aspartate polymers and right-handed for alkyl esters with longer side chains, while experimentally it is found that only the methyl L-aspartate polymer is in the left-handed form. Clearly, the parameters used in these calculations could be adjusted slightly to give agreement between observed and calculated helix senses. Such an adjustment may also produce a reorientation of the side chain to agree with the experimental results.

That the side-chain orientations can depend on the length of the side chain is shown by the comparison of poly(β-benzyl L-aspartate) with poly(β-methyl L-aspartate). Although both polymers favor left-handed helices, the side-chain conformations are markedly different. Using the criterion given above for describing the side-chain orientation, *i.e.*, the direction of the C–C line in the ester C–O–C group, it is clear, however, that the orientation of methyl L-aspartate must also be described as transverse rather than longitudinal as predicted. The orientation of left-handed benzyl L-aspartate side chain is also transverse.

Although there is some general agreement between the observed and calculated behavior of side-chain conformations, when a detailed comparison of the orientations is made, discrepancies are found which extend throughout the length of the side chain, including the $C_\beta H_2$ group. This is not completely unexpected, since the theoretical calculations apply to isolated molecules *in vacuo* and it would be surprising if the packing of such molecules into the solid state did not result in a modification to their side-chain conformations to allow a minimum of the packing energy. A full comparison of experimental and predicted side-chain conformations must therefore await calculations of conformation in the solid state.

Acknowledgments. This work is supported by the Science Research Council of Great Britain. We are grateful to Professor H. A. Scheraga for providing the atomic coordinates of the predicted Rt(−), Rl(−), Lt(−), and Ll(+) side-chain conformations for both poly(β-benzyl L-aspartate) and poly(β-methyl L-aspartate).

Thermodynamic Interaction in Polydimethylsiloxane–Hydrocarbon Systems from Gas–Liquid Chromatography

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ABSTRACT: Polydimethylsiloxane has been used as the stationary phase in gas–liquid chromatography. Retention volumes have been used to calculate the thermodynamic interaction parameters for a series of linear and branched alkanes and aromatic hydrocarbons interacting with the polymer. Values of the χ parameter have been compared with results for the same systems obtained from equilibrium (static) vapor-absorption experiments, and found to be in excellent agreement. The successful comparison indicates the potential value of the glc route as the source of rapidly obtained thermodynamic data at infinite dilution of the volatile phase. A number of the prerequisites are established for useful application of the glc method to polymer solution thermodynamics.

Numerous recent studies of gas–liquid chromatography (glc)[1-3] have established the method as a rapid and consistent means of determining thermodynamic functions for nonelectrolyte systems. The primary datum obtained by this flow method is the activity coefficient (γ_1^∞) of a volatile solute at Infinite dilution. This is related experimentally to the specific retention volume V_g^0 of the solute by a nonvolatile solvent (liquid or solid) in the stationary phase, through the equation

$$\gamma_1^\infty = RT/V_g^0P_1^0M_2 \qquad (1)$$

where M_2 is the solvent molecular weight and P_1^0 is the solute saturation vapor pressure.

Application of the method to polymeric solvents would represent a very convenient means of determining thermodynamic data at very high polymer concentrations, a region which is of inherent interest from both theoretical and applied points of view. Guillet and coworkers[4] have anticipated the

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(1) (a) D. H. Everett and C. T. H. Stoddard, *Trans. Faraday Soc.*, **57**, 746 (1961); (b) A. J. Ashworth and D. H. Everett, *ibid.*, **56**, 1609 (1960).

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

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

(4) (a) O. Smidsrød and J. E. Guillet, *Macromolecules*, **2**, 272 (1969); (b) D. G. Gray and J. E. Guillet, *ibid.*, **4**, 129 (1971); (c) J. E. Guillet and A. N. Stein, *ibid.*, **3**, 102 (1970).

use of glc with polymers, referring to the application as a "molecular probe technique" and showing its value as a rapid route to glass transitions, melting ranges, and crystallinity effects in various polymers. The general validity of thermodynamic data calculated from glc results is open to a number of questions, however, and these have been reviewed fully by Young.[5] Perhaps the most serious of these questions concerns the dynamic nature of the measurement, and hence the question of whether equilibrium conditions of solute–solvent interaction are attained. For the specific case of polymer solvents, two additional complications arise: first, the appearance in eq 1 of a polymer molecular weight term, which may be difficult to specify for polydisperse materials, and second, the difficulty of establishing the significance of an activity coefficient in polymer solutions. We have considered the latter objections in an earlier publication[6] and proposed solutions which are applied here to a test of the glc method as a source of thermodynamic data for polydimethylsiloxane (PDMS) systems at infinite dilution of various hydrocarbon solutes. Hopefully, the present results should stimulate a rapid expansion of experimental information in hitherto unscanned concentration limits of polymer solutions.

The interaction parameter data for PDMS–hydrocarbon systems have been determined over an appreciable temperature range, and a number of the results are compared here with corresponding thermodynamic interaction parameters obtained from equilibrium vapor-sorption data by Kao, *et al.*[7] Their results cover broad concentration ranges and were therefore readily extrapolated to infinite dilution of the absorbing vapor. Further, the possible influence of some experimental variables in the glc method on the data derived from it is examined.

Experimental Section

Stationary Phase and Column Description. A single PDMS polymer has been used as the solvent in the reported work. The polymer, also used and characterized by Chahal and coworkers,[7] had a viscosity-average molecular weight of 5×10^6. Column preparation procedures followed the methods of Tewari, *et al.*,[8] the polymer being coated onto Chromosorb W support (60–80 mesh acid washed, DMCS treated) from solutions in *n*-hexane. The coated support was resieved and packed into 4-ft, 0.25-in. o.d. copper tubing which had previously been washed in methanol. The exact weight of solvent on support was evaluated in triplicate, by 72 hr of Soxhlet extraction (*n*-hexane) using a ceramic thimble. A total of four columns were prepared. Details of these are given in Table I. Column I (uncoated support) was used to monitor interactions between solutes and support, columns II–IV were used to study the elution effects in PDMS–hydrocarbons and to detect possible changes in retention volumes due to varying solvent–support ratios. The height-equivalent theoretical plate number (HETP) is based on elution peaks for 2-methylhexane, using the procedure of van Deemter.[9]

Solutes. In various portions of this work, 13 hydrocarbon solutes were used. A number of the materials were identical with those used by Chahal, *et al.*,[7] in their equilibrium absorption work, although 2-methylbutane (item 5^1 in Table II) was only used at column temperatures of 25° in our work. At higher temperatures, 2-methylpentane (item 5) was preferred because of its more convenient vapor pressures at the higher experimental temperatures; this material had not been part of the earlier absorption program. The equations of state for these solutes are known, making possible accurate evaluation of physical properties for the pure compounds. For simplicity the solutes are coded numerically according to the scheme of Table II.

TABLE I
DESCRIPTION OF COLUMNS

Code	I	II	III	IV
Length, ft	4	4	4	4
Chromosorb W, g	5.3400	5.9308	6.4317	6.2128
PDMS, g	0	0.3703	0.4953	0.7505
Wt % PDMS	0	6.21	7.70	10.78
HETP		560	680	910

TABLE II
SOLUTE DESCRIPTION AND CODE

Code no.	Compound	Code no.	Compound
1	*n*-Pentane	6	2-Methylhexane
2	*n*-Hexane	7	2-Methylheptane
3	*n*-Heptane	8	2,2,4-Trimethylpentane
4	*n*-Octane	9	Benzene
5	2-Methylpentane	10	Toluene
5^1	2-Methylbutane	11	*p*-Xylene
		12	Ethylbenzene

Apparatus and Procedure. The dual column glc apparatus consisted of a Perkin-Elmer hot-wire thermal conductivity detector (Model 008-0686); column temperature was controlled in a water bath, regulated to ±0.05° by a Haake Model E.D. unit. Experimental temperatures extended from 25 to 70°. In this range, the solvent (polymer) vapor pressure is negligible. Helium was used as the carrier gas, minimizing solution effects in the solvent.[10]

Flow rates in the range 70–120 ml/min were measured at room temperature by a soap-bubble flowmeter at the detector outlet, and were chosen so as to indicate any flow-rate dependence of elution peaks, at the same time leading to convenient operation of the columns. Inlet pressure was controlled by precision regulators (Negretti-Zambra R/182, *viz.*, also the apparatus of Tewari, *et al.*[8]) and measured on mercury manometers with a range up to 1500 mm. Inlet pressures were generally in the range 900–1200 mm, while the outlet pressure was always atmospheric. Solutes were injected through Hamilton injection ports (Model 86800) using 10-μl Hamilton syringes and techniques described by Tewari.[8] In this procedure conditions of infinite dilution of solute are approximated by introducing vapor–air mixtures, the solute volumes being of the order of nanoliters.

Uniformly symmetrical elution peaks obtained by these injection procedures were considered to confirm the infinite dilution approximation[11] and thus to represent solvent–solute equilibrium interactions. Frequent checks failed to indicate any dependence of retention times on size of the injected sample when this was increased by about an order of magnitude, thus paralleling the findings of Guillet.[4c] The present system clearly is not greatly susceptible to adsorption problems, provided adequate amounts of polymer are supported, but we believe adsorption effects to be responsible for the pattern of results generated from column II as discussed later.

Evidently, in keeping with the recent admonition of Conder,[12] peak asymmetry is not a necessary condition for surface adsorption effects. The absence of asymmetry, however, resolved difficulties of choice in defining a suitable working value of the retention

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

(6) D. Patterson, Y. B. Tewari, H. P. Schreiber, and J. E. Guillet, *Macromolecules*, **4**, 356 (1971).

(7) W. P. Kao, R. S. Chahal, and D. Patterson, manuscript in preparation.

(8) Y. B. Tewari, D. E. Martire, and J. P. Sheridan, *J. Phys. Chem.*, **74**, 2345 (1970).

(9) H. Purnell, "Gas Chromatography," Wiley, New York, N. Y., 1962, Chapter 8.

(10) D. H. Desty, A. Goldup, G. R. Luckhurst, and W. T. Swanton, "Gas Chromatography," Butterworths, London, 1962.

(11) J. R. Conder, *J. Chromatogr.*, **39**, 273 (1969).

(12) J. R. Conder, *Anal. Chem.*, **43**, 367 (1971).

TABLE III
SPECIFIC RETENTION VOLUMES FOR
PDMS–HYDROCARBON SYSTEMS

Solute	V_g^0, ml/g, from columns III and IV 25°	40°	55°	70°
1	74.76	43.65	27.43	18.33
2	211.1	114.8	66.45	41.05
3	587.6	290.8	157.8	89.54
4	1626.6	740.9	367.1	194.9
5	149.9	83.9	51.63	32.21
5[1]	58.39			
6	420.9	211.4	119.6	70.04
7	1138.0	534.7	275.8	150.1
8	510.2	260.9	145.8	84.66
9	340.4	181.2	105.4	63.43
10	959.6	463.7	251.4	141.3
11	2654.6	1187.5	586.5	307.4
12	2365.7	1090.5	541.2	286.4

volume. In this work we have followed the recommendations of Cruickshank, Windsor, and Young[3a] in defining the retention volume by the elution peak maximum.

Results and Discussion

Specific Retention Volumes. The solute specific retention volumes reported in Table III were calculated from corrected peak retention times and column operating conditions, using the well-known expression of Littlewood and coworkers.[13] Experimental details were very similar to those described in ref 8. Retention time used in the calculation of specific retention volumes was an average of three runs. Thus, the reported values of V_g^0 for columns III and IV (*viz.*, Table III) are an average of at least nine measurements (two loadings and two flow rates). Individual values were found to vary by no more than 1% in all cases. Results from column II are treated separately; these were distinctly higher and somewhat more so at lower temperatures, in spite of the fact that elution peaks appeared to be perfectly symmetric. We conclude therefore that retention characteristics in our experimental systems are independent of the solvent/support ratio when this exceeds a value of about 0.065, but that a distinct effect, tentatively associated with solute/support interaction, is observed at lower values of that ratio. This subject is discussed further later on. The V_g^0 values from columns III and IV appear to be free of systematic errors arising from such experimental variables as injection volume, gas flow rate, and inlet pressure. Further, they meet the criteria of infinite dilution approximations, and their independence on solvent/support ratio coupled with absence of peak asymmetry makes them acceptable[5] for calculations of thermodynamic parameters.

Thermodynamic Interaction Parameters. The link between experimental glc data and the thermodynamics of solvent–solute interaction for the case of a polymeric solvent have been considered in some detail earlier.[6] No unique expression can be given for this relationship, since its form will depend on the model chosen to calculate the combinatorial entropy of mixing for the pair. Generally, two models are favored. The familiar Flory–Huggins (lattice) approximation to polymer solutions leads to the statement[6]

$$\chi = \ln\left[\frac{273.2Rv_2}{V_g^0 V_1 P_1^0}\right] - \left[1 - \frac{V_1}{M_2 v_2}\right] - \frac{P_1^0}{RT}\,(B_{11} - V_1) \quad (2)$$

where V_1 is the molar volume of pure (liquid) solute, P_1^0 is its vapor pressure at T°K, v_2 is the specific volume of polymer solvent, B_{11} is the gas-state second virial coefficient of the solute, R has its usual significance, and χ is the Flory–Huggins free energy of mixing (interaction) parameter. In more recent theory,[14] the concept of volume fractions has been replaced by the temperature-independent "core" or "hard-core" volumes of components, leading to the analogous expression[6]

$$\chi^* = \ln\left[\frac{273.2Rv_2^*}{V_g^0 V_1^* P_1^0}\right] - \left[1 - \frac{V_1^*}{M_2 v_2^*}\right] - \frac{P_1^0}{RT}\,(B_{11} - V_1) \quad (3)$$

where the starred quantities differentiate the hard-core volumes of solvent and solute from molar quantities. Both eq 2 and 3 are approximations. They assume that cross-term virial coefficients arising from carrier gas–solvent interactions may be neglected and, similarly, that solute–carrier gas interactions in the gas phase have a negligible effect on the measured V_g^0. In fact, these approximations are justified by operating at inlet pressures only slightly above atmospheric, by choosing He as the carrier gas, and by restricting work to nonpolar solutes with limited tendency for specific (nondispersion force) interactions with the polymer. Nevertheless, from a formal point of view, their introduction restricts the accuracy of the calculated free energy parameters.[3b] A further approximation reduces the second term of eq 2 and 3 to −1, a justifiable procedure when a high molecular weight (polymer) solvent is involved.

In our computation of χ and χ^*, virial coefficients were calculated from the corresponding state equations of McGlashan and Potter,[15] using critical constants taken from Dreisbach.[16] This source was also used for Antoine constants to calculate vapor pressure values (P_1^0), while the hard-core data are those of Flory[14] and Morimoto.[17] Further approximations had to be introduced for the calculations, the results of which are given in Table IV. It was assumed that the hard-core parameters V_1^* and V_2^* are fully independent of temperature,[18] allowing use of their known values at 25° in calculating χ^* at the higher exprimental temperatures. Furthermore, in order to compare glc- and absorption-derived χ^* data at 25°, approximations were needed in the cases of *n*-octane, *p*-xylene, and ethylbenzene (solutes 4, 11, and 12 in Table IV), for which accurate experimental P_1^0 values are not available at that low temperature.

The comparison of our χ^* values with those obtained from vapor-sorption equilibria [$(\chi^*)_{abs}$ in Table IV] indicates very good agreement in all cases. It is evident that glc represents a very rapid, convenient experimental route to thermodynamic interaction measurements in polymer systems at the limit of infinite dilution of the low molecular weight solute. In the present cases, data match the validity of those derived from more conventional but laborious static methods, but it would seem premature to claim this level of agreement generally for all polymeric stationary phases. The readily adjusted temperature environment of the supported polymer solvent further adds to the usefulness of the method. As shown previously,[6]

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(13) A. B. Littlewood, C. S. G. Phillips, and D. T. Price, *J. Chem. Soc.*, 1480 (1955).

(14) (a) R. A. Orwoll and P. J. Flory, *J. Amer. Chem. Soc.*, **89**, 6814 (1967); (b) R. A. Orwoll and P. J. Flory, *ibid.*, **89**, 6822 (1967); (c) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035 (1968).

(15) M. L. McGlashan and D. J. B. Potter, *Proc. Roy. Soc., Ser. A*, **267**, 478 (1962).

(16) R. R. Dreisbach, *Advan. Chem. Ser.*, **No. 15** (1955); **No. 22** (1959); **No. 29** (1961).

(17) S. Morimoto, *Makromol. Chem.*, **133**, 197 (1970).

(18) Reservations exist on this point. These are discussed in a separate forthcoming publication.

TABLE IV
SUMMARY OF χ AND χ^*. COMPARISON WITH RESULTS FROM ABSORPTION MEASUREMENTS

	25°			40°		55°		70°	
Solute	χ	χ^*	$(\chi^*)_{abs}$	χ	χ^*	χ	χ^*	χ	χ^*
1	0.409	0.513	0.51	0.433	0.541	0.437	0.561	0.430	0.557
2	0.448	0.524		0.446	0.529	0.449	0.539	0.447	0.545
3	0.497	0.556	0.53	0.496	0.560	0.481	0.551	0.491	0.566
4	0.556^a	0.600^a	0.57	0.542	0.589	0.535	0.586	0.537	0.594
5	0.449	0.534		0.450	0.541	0.419	0.518	0.431	0.538
5^1	0.392	0.440	0.48						
6	0.461	0.520		0.479	0.543	0.452	0.522	0.457	0.531
7	0.521	0.566		0.513	0.562	0.498	0.551	0.504	0.561
8	0.446	0.499	0.47	0.441	0.498	0.442	0.485	0.430	0.498
9	0.814	0.864	0.87	0.792	0.848	0.755	0.816	0.746	0.812
10	0.802	0.833	0.82	0.797	0.831	0.758	0.795	0.753	0.793
11	0.800^a	0.822^a	0.80	0.797	0.820	0.775	0.800	0.772	0.799
12	0.828^a	0.833^a	0.80	0.810	0.832	0.789	0.814	0.778	0.804

^{a} From extrapolations of P_1^0 to 25°.

the heat of dilution of solute (component 1) at infinite dilution can be obtained from the temperature dependence of the interaction parameter, the relevant expression being particularly simple when χ^* is involved, *viz.*

$$\Delta \bar{h}_1^\infty = R(\partial\chi^*/\partial 1/T) \qquad (4)$$

The range of applicability of this route to more detailed solution thermodynamics is uncertain, however. In the present systems, free of strong polar-force interactions, the temperature dependence of both χ and χ^* is too small to be detected with sufficient accuracy, but recent results of Newman and Prausnitz[19] indicate that more success may be expected in systems with stronger specific interactions.

It is not a primary purpose of this paper to interpret the significance of the absolute interaction parameter values quoted in Table IV. The results for both χ and χ^* are given at all experimental temperatures because it is not evident *a priori* which of the two parameters reflects the more relevant theoretical approach to polymer solution thermodynamics. By way of further commentary, we note the recent work of Flory and collaborators[14c] who express χ^* at zero pressure and infinite dilution as the sum of contributions from equation of state and contact interaction concepts

$$\chi^* RT = P_1^* V_1^* \times \left\{\left(3\tilde{T}_1 \ln \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_2^{1/3} - 1} + \tilde{v}_1^{-1} - \tilde{v}_2^{-1}\right) + \frac{X_{12}}{P_1^* \tilde{v}_2}\right\} \qquad (5)$$

where $(\tilde{v})^{1/3} = 1 + \alpha T/3(1 + \alpha T)$, $\tilde{T} = T/T^* = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3}$, and α is the thermal expansion coefficient. $\tilde{v}$ and $\tilde{T}$ are reduced quantities and asterisked quantities are the reduction parameters.[14a] The first term of eq 5 is the equation of state contribution arising from differences in the thermal expansion coefficients (α) of the solute–solvent pair. The second term arises from potential differences in the components and introduces the contact interaction parameter X_{12}.

TABLE V
CONTACT INTERACTION PARAMETER (X_{12}) IN PDMS
($\tilde{v}_2 = 1.224$) AT 25°

Solute	$\tilde{T}_1 \times 10^2$	$\tilde{v}_1$	P_1^*, cal/cm^3	X_{12}, cal/cm^3	X_{12} (ref 17), cal/cm^3
1	7.170	1.3607	97.17	2.88	1.1
2	6.715	1.3215	101.3	2.93	1.1
3	6.425	1.2987	103.2	2.99	1.4
4	6.147	1.2783	103.5	3.35	1.6
5	6.850	1.3329	97.11	2.87	
6	6.422	1.2993	95.41	2.78	
7	6.179	1.2808	94.57	2.82	
8	6.323	1.2913	91.76	2.40	
9	6.330	1.2917	152.3	8.33	5.6
10	5.933	1.2633	134	6.91	3.5
11	5.741	1.2504	127	5.93	2.0
12	5.732	1.2498	130	6.03	1.8

Values of the parameter X_{12} have been calculated for the present PDMS–solute systems and listed in Table V. The last column of this table lists X_{12} values read from graphical representations by Morimoto.[17] His data derive from heats of mixing at infinite dilution of the polymer and are therefore at the opposite concentration limit to ours. Absolute comparison of the two sets of X_{12} values is further compromised, since in the heat of dilution route the adjustable parameter S_2/S_1 (ratio of the number of contact sites) must be specified. Specification of contact sites is not involved in the glc measurements which therefore yield a more accurate X_{12} datum.

On a comparative basis, however, the trends shown in Morimoto's and our data are similar. Thus, contact interactions between *n*-alkanes and PDMS increase with increasing chain length of the alkanes. Further, in both sets X_{12} decreases as the alkyl group in alkylbenzenes increases in size.

Semiquantitative Uses of Glc Data. The sensitivity of thermodynamic data obtained from glc to vapor pressures of the solute phase, inherent in the statements of eq 2 and 3, has been noted more generally in a preceding publication.[6] In order to illustrate the contribution of the virial coefficient B_{11} to values of χ, we have computed the ratio of χ (χ^*), calculated according to eq 2 and 3, to the value obtained by omitting the virial coefficient term from the equations. The results at 25 and 70° are presented in Table VI. The pattern of results follows expectations in showing the diminished correctness of the ideality assumption at the higher temperature and the apparent direct dependence of the ratios on absolute vapor pressures at the experimental temperatures. Neglect of the correction affects χ^* only slightly less severely than χ. A recommendation arising out of the comparison would call for the use of the virial coefficient term if accuracy better than 5% in χ was required and the solute vapor pressure in the relevant glc experiment exceeded $P_1^0 = 200$ mm.

(19) R. Newman and J. M. Prausnitz, manuscript in preparation.

TABLE VI
IMPORTANCE OF NONIDEALITY VAPOR PRESSURE CORRECTION IN CALCULATION OF THERMODYNAMIC PARAMETERS[a]

	25°			70°		
Solute	P_1^0, mm	χ_{ratio}	χ^*_{ratio}	P_1^0, mm	χ_{ratio}	χ^*_{ratio}
1	512.5	1.096	1.075	2123.00	1.287	1.208
2	151.2	1.037	1.031	790.5	1.134	1.108
3	45.72	1.014	1.013	303.6	1.063	1.054
4	13.98[b]	1.005	1.007	119.0	1.031	1.029
5	221.7	1.051	1.043	1025	1.177	1.137
6	65.88	1.022	1.019	402.1	1.088	1.075
7	20.61	1.009	1.009	159.5	1.043	1.039
8	49.34	1.023	1.018	305.8	1.091	1.078
9	95.18	1.012	1.012	550.9	1.046	1.042
10	28.44	1.006	1.006	203.8	1.026	1.024
11	8.85[b]	1.002	1.002	78.75	1.014	1.014
12	9.89[b]	1.002	1.001	84.75	1.013	1.013

[a] Ratios are corrected/uncorrected values as calculated from eq 2 and 3. [b] Extrapolated values.

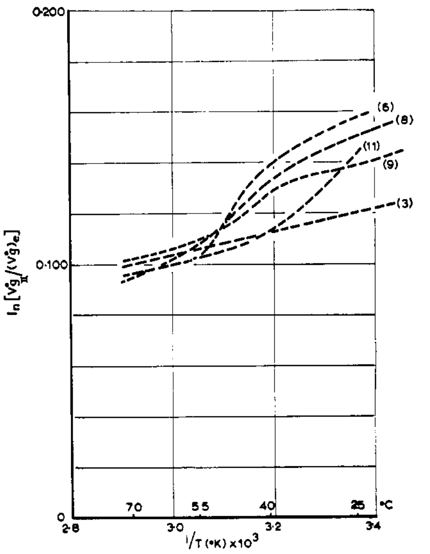

Figure 1. Temperature variation of retention volume ratio.

Column II *vs.* Columns III and IV. As noted previously, the retention volumes for all solutes calculated for column II were found to be consistently greater than those obtained from retention volumes in columns III and IV. The arguments advanced in support of the contention that data from columns III and IV represent equilibrium interactions at the solute–polymer interface are confirmed by the close agreement between the interaction parameter values calculated from these results and the χ^* obtained from static equilibrium vapor-sorption results. Thus, the $(V_g^0)_{II}$ data were affected by experimental artifacts. A reasonable suggestion seems to be adsorption of the solute on uncoated support. Numerous authors have commented on the problem of adsorption in glc measurements,[20] and the development of inert supports has been an active feature of the glc scene. In principle, Chromosorb W, used in this work, is an "inert" support, and control runs with column I showed no obvious adsorption effects. Recently, however, Meyer and Ross have reported[21] that adsorption effects have been detected on this substrate; indeed, in a current paper, Conder[12] indicates that adsorption effects have occurred even with the use of polytetrafluoroethylene as the support medium.

The assumption that $(V_g^0)_{II} > (V_g^0)_e$ (where $(V_g^0)_e$ is the equilibrium datum of columns III and IV) because of adsorption effects calls for an inverse temperature dependence of the effect. Examination of the ratio $[(V_g^0)_{II}/(V_g^0)_e]$ reveals a tendency for such a dependence, albeit a nonsystematic one. Excepting a few deviations from the pattern, the general variation is indicated in Figure 1 for systems 3, 6, 8, 9, and 11. The rather complex curves give a qualitative activation energy of the order of 0.5 kcal/mol, a value which is not unreasonable for physisorption at the free support surface.

Conclusions

Close agreement has been found between thermodynamic interaction parameter values for PDMS–hydrocarbon systems obtained by the rapid, dynamic glc method and those obtained from static, equilibrium absorption data.

The successful comparison should promote rapid accumulation of thermodynamic data in the important concentration range near infinite polymer concentration.

Complete coverage of supporting surfaces by the stationary phase is necessary if elution data are to be free of influence from adsorption effects. In the present case (PDMS on Chromosorb W), this degree of coverage is attained at polymer/support weight ratios exceeding 0.07.[22]

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(20) (a) R. L. Martin, *Anal. Chem.*, **33,** 347 (1961); (b) D. E. Martire, R. L. Pecsok, and J. H. Purnell, *Trans. Faraday Soc.*, **61,** 2495 (1965).

(21) E. F. Meyer and R. A. Ross, *J. Phys. Chem.*, **75,** 831 (1971).

(22) Readers are referred to an analogous gas–liquid chromatographic investigation of solution thermodynamics involving alkanes in polyisobutylene, which only recently came to our attention, *viz.*, W. E. Hammers and C. L. De Ligny, *Recl. Trav. Chim. Pays Bas*, **90,** 912 (1971).