Notes

Interlaboratory Comparison of Gas-Liquid Chromatographic Data for Polydimethylsiloxane-Hydrocarbon Systems

R. N. LICHTENTHALER,[1a] J. M. PRAUSNITZ,[1a]
C. S. SU,[1b] H. P. SCHREIBER,[1b] and D. PATTERSON*[1b]

Department of Chemical Engineering, University of California, Berkeley, Berkeley, California, and Department of Chemistry, McGill University, Montreal, Quebec, Canada.
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The systems (PDMS)-hydrocarbons have been examined independently by two groups of workers[2a,b] using the gas-liquid chromatographic (glc) technique. In the initial publication from the McGill laboratory,[2a] it was shown that thermodynamic interaction parameters χ^* calculated from the V_g^0 values were in good agreement with values[3] obtained from the conventional, equilibrium sorption method. The V_g^0 values obtained in the Berkeley laboratory for PDMS interacting with n-C_5, n-C_6, benzene, and toluene at 25, 40, and 55° are higher than the McGill data, the difference varying from 6.1 to 11.6%. The higher V_g^0 values would result in χ^* being some 0.06–0.11 lower than the sorption-derived values, and therefore outside the range of combined experimental errors claimed for these techniques. As a result of these discrepancies we have carried out an interlaboratory comparison of V_g^0 data, in which polymer samples were exchanged, packed columns were interchanged, and implicitly the performances of the two sets of apparatus and their operators have been compared. Here, we briefly comment upon the results of this intercomparison shown in Table I.

The intercomparison of data, columns A–F, shows that apparently none of the variables involved, *viz.*, the polymer sample, exact apparatus-operator combination, or age of packed column seriously affects the V_g^0 data, except the coating and packing procedure. That is indicated by the agreement of the results in column D with those in column E and the agreement of those of columns B, C, and F with each other. Both groups obtain the same results (to within ±1.5% about a mean) using the same chromatographic column, whereas the results with the Berkeley column are always somewhat higher (about 2%) than those with the McGill column. However the study has not fully resolved the discrepancy with the results in column A. The bulk of the glc data remains higher than the results of Summers *et al.* by 3–5%. These earlier data at 25° are supported by χ^* data obtained through the apparently accurate vapor sorption method.[3] A choice of absolute V_g^0 values is for this reason difficult. It is possible that fuller comparison of glc-derived and equilibrium sorption-derived χ^* for PDMS-hydrocarbons would be useful.

Table I
Interlaboratory Comparison of V_g^0 Data for PDMS

°C	A[a]	B	C	D	E	F
25 (1)[b]	74.76	76.8–78.8	75.2–77.1	77.8–79.5	79.9–81.0	77.2
(2)	211.1	214.8–220.6	210.5–217.4	219.2–224.2	226.4–230.4	219.9
(6)	340.4	348.4–356.7	342.0–353.6	353.3–372.0	366.8–380.0	354.1
40 (1)	43.65	46.6–47.1	45.8–46.5	47.3–48.1	47.1–48.6	46.1
(2)	114.8	119.2–120.2	118.9–120.0	123.2–123.9	123.0–126.8	120.0
(3)	290.8	305.0–307.0	303.7–308.3	312.8–318.2	316.7	307.6
(5)	463.7	493.3–494.4	492.4–504.9	508.5–520.8	504.8–525.1	494.1
(6)	181.2	191.1–191.9	190.1–192.5	197.3–198.2	196.2–203.3	192.9
55 (1)	27.43	29.3–29.4	29.4–30.1	29.9	29.7–29.8	29.2
(2)	66.45	70.1–70.2	70.2–70.8	72.6	70.5–72.1	70.6
(3)	157.8	164.3–165.3	165.3–166.6	168.4	169.5	165.6
(4)	367.1	385.8–386.4	385.9–388.5	398.9	395.3	
(5)	251.4	263.0–263.5	264.0–266.0	267.3	268.4–269.2	264.6
(6)	105.4	110.0–110.1	110.7–111.0	113.1	111.6–112.5	110.1

[a] For columns, see A, results of Summers *et al.*;[2a] B, recent McGill results using samples of ref 1a; C, recent McGill results using PDMS sample of Berkeley group.[2b] Range indicates results obtained in repeated trials over a 2-month period; D, recent McGill results using column packed by the Berkeley group with their PDMS sample; E, results reported in ref 2b; F, results of Berkeley group using column packed by the McGill group. [b] For probes, see (1) n-C_5; (2) n-C_6; (3) n-C_7; (4) n-C_8; (5) toluene; (6) benzene.

(1) (a) From the University of California at Berkeley; (b) from McGill University.
(2) (a) W. B. Summers, Y. B. Tewari, and H. P. Schreiber, *Macromolecules*, 5, 12 (1972). (b) R. N. Lichtenthaler, R. D. Newman, and J. M. Prausnitz, *Macromolecules*, 6, 650 (1973).
(3) R. S. Chahal, W. P. Kao, and D. Patterson, *J. Chem. Soc., Faraday Trans. I*, 69, 1834 (1973). In this publication, the interaction parameter is written without an asterisk. In conformity with recent usage, it is obtained using segment fraction, not volume fraction, as the composition variable. Reference 2a uses both volume and segment fraction, employing χ and χ^* as the symbols for the parameters so derived.

Comments on the Paper "Nuclear Magnetic Resonance Studies on the Polymerization of Cyclic Ethers"[1] by G. Pruckmayr and T. K. Wu

KRZYSZTOF MATYJASZEWSKI and
STANISŁAW PENCZEK*

Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Łódź 40, Poland.
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Recently Pruckmayr and Wu published a paper entitled "Nuclear Magnetic Resonance Studies on the Polymeriza-

(1) G. Pruckmayr and T.-K. Wu, *Macromolecules*, 6, 33 (1973).