**Notes**

CHROM. 6230

## Estimation of critical volumes from the response of the gas chromatographic thermal conductivity detector

In gas chromatography, relative molar response ($RMR$) factors are commonly utilized to obtain the most accurate quantitative data with the thermal conductivity (TC) detector and helium as carrier gas[1]. The main features of these peak area-correction factors are that they are invariable over a wide range of experimental parameters such as flow-rate, detector temperature and type[2]. Several publications by BARRY AND ROSIE[3-5] have recently appeared on the prediction of $RMR$ factors for the TC detector. These authors employed the "molecular diameter" approach originally proposed by LITTLEWOOD[6] in order to predict successfully $RMR$ data for nearly 150 compounds with helium as carrier gas. Our $RMR$ equation which can accurately accommodate both non-polar and polar compounds may be written as

$$RMR_i = \left[\frac{\sigma_i + \sigma_1}{\sigma_\phi + \sigma_1}\right]^2 \left[\frac{M_i - M_1}{M_\phi - M_1}\right]^{\ddagger} \times 100 \qquad (1)$$

where $\sigma$ and $M$ indicate molecular diameter and molecular weight, respectively. The subscripts $i$, $\phi$, and $1$ refer to the chromatographic solute under consideration, the

TABLE I

PREDICTED $RMR$ DATA FOR POLAR SUBSTANCES WITH HELIUM AS CARRIER GAS

| Compound | $RMR_{exptl.}$[a] | $RMR_{predicted}$ | $V_c$[b] | Mol. wt. |
|---|---|---|---|---|
| Methanol | 55 | 57 | 118 | 32.0 |
| Ethanol | 72 | 73 | 167 | 46.1 |
| Propanol | 86 | 87 | 218 | 60.1 |
| Butanol | 99 | 101 | 274 | 74.1 |
| Ethyl acetate | 108 | 107 | 286 | 88.1 |
| Isopropyl acetate | 121 | 120 | 336 | 102 |
| Butyl acetate | 135 | 133 | 395 | 116 |
| Isoamyl acetate | 145 | 144 | 446 | 130 |
| Acetone | 86 | 85 | 211 | 58.1 |
| Methyl ethyl ketone | 98 | 99 | 267 | 72.1 |
| Acetonitrile | 70 | 72 | 173 | 41.1 |
| Carbon disulfide | 86 | 86 | 170 | 76.1 |
| Methylene chloride | 94 | 91 | 193 | 89.9 |
| Chloroform | 108 | 104 | 240 | 119 |
| Carbon tetrachloride | 120 | 122 | 276 | 154 |
| 1,1-Dichloroethane | 103 | 102 | 244 | 99.0 |
| Dibromomethane | 107 | 106 | 235 | 174 |

[a] Abstracted from refs. 3-5.
[b] Critical volumes tabulated by REID AND SHERWOOD[8].

internal standard (benzene) and the carrier gas (helium), respectively. The factor of 100 represents the response of benzene arbitrarily assigned a value of 100 response units per mole.

TABLE II

ESTIMATED CRITICAL VOLUMES FOR POLAR SUBSTANCES

| Compound | RMR[a] | Mol. wt. | Estimated $V_c$ (ml/gmole) |
|---|---|---|---|
| Pyrrole | 86 | 67 | 198 |
| Hexylamine | 104 | 101 | 242 |
| Ethylene oxide | 58 | 44 | 95 |
| Propylene oxide | 80 | 58 | 181 |
| Methyl mercaptan | 59 | 48 | 93 |
| Ethyl mercaptan | 87 | 62 | 214 |
| Tetrahydrofuran | 83 | 72 | 173 |
| Acetaldehyde | 65 | 44 | 129 |
| | | | |
| Pyrroline | 83 | 69 | 178 |
| Pyrrolidine | 91 | 71 | 219 |
| Pyridine | 100 | 79 | 260 |
| 1,2,5,6-Tetrahydropyridine | 103 | 83 | 266 |
| Acrylonitrile | 78 | 53 | 181 |
| Propionitrile | 84 | 55 | 213 |
| n-Butyronitrile | 105 | 69 | 314 |
| Aniline | 114 | 93 | 316 |
| Piperidine | 102 | 85 | 260 |
| | | | |
| 3-Hexanone | 123 | 100 | 361 |
| 2-Hexanone | 130 | 100 | 409 |
| 3,3-Dimethyl-2-butanone | 118 | 114 | 306 |
| Methyl n-amyl ketone | 133 | 114 | 405 |
| Methyl n-hexyl ketone | 147 | 128 | 469 |
| Cyclopentanone | 106 | 84 | 285 |
| Cyclohexanone | 125 | 98 | 383 |
| 2-Nonanone | 161 | 142 | 541 |
| Methyl isobutyl ketone | 118 | 100 | 327 |
| Methyl isoamyl ketone | 138 | 114 | 441 |
| | | | |
| 3-Methyl-1-pentanol | 107 | 86 | 284 |
| 2-Pentanol | 110 | 88 | 303 |
| 3-Pentanol | 109 | 88 | 297 |
| 2-Methyl-2-butanol | 106 | 88 | 278 |
| n-Hexanol | 118 | 102 | 320 |
| 3-Hexanol | 125 | 102 | 366 |
| 2-Hexanol | 130 | 102 | 400 |
| n-Heptanol | 128 | 116 | 362 |
| Cyclopentanol | 109 | 86 | 297 |
| Cyclohexanol | 112 | 100 | 289 |
| Ethyl acetate | 111 | 88 | 310 |
| Isopropyl acetate | 121 | 102 | 347 |
| n-Butyl acetate | 135 | 116 | 410 |
| n-Amyl acetate | 146 | 130 | 462 |
| Isoamyl acetate | 145 | 130 | 455 |
| n-Heptyl acetate | 170 | 158 | 578 |

TABLE II *(continued)*

| Compound | $RMR^a$ | Mol. wt. | Estimated $V_c$ (ml/gmole) |
|---|---|---|---|
| Diisopropyl ether | 130 | 102 | 409 |
| Di-*n*-propyl ether | 131 | 102 | 417 |
| Ethyl *n*-butyl ether | 130 | 102 | 409 |
| Di-*n*-butyl ether | 160 | 130 | 566 |
| Di-*n*-amyl ether | 183 | 158 | 677 |
| 1-Chlorobutane | 111 | 93 | 297 |
| 2-Chlorobutane | 109 | 93 | 284 |
| 1-Chloro-2-methylpropane | 108 | 93 | 277 |
| 2-Chloro-2-methylpropane | 104 | 93 | 254 |
| 1-Chloropentane | 123 | 107 | 346 |
| 1-Chlorohexane | 134 | 121 | 395 |
| 1-Chloroheptane | 147 | 135 | 460 |
| Bromoethane | 98 | 109 | 220 |
| 1-Bromopropane | 108 | 123 | 233 |
| 2-Bromopropane | 108 | 123 | 233 |
| 1-Bromobutane | 119 | 137 | 276 |
| 2-Bromobutane | 116 | 137 | 260 |
| 1-Bromo-2-methylpropane | 115 | 137 | 254 |
| 1-Bromopentane | 128 | 151 | 309 |
| Iodomethane | 96 | 142 | 158 |
| Iodoethane | 106 | 156 | 191 |
| 1-Iodopropane | 117 | 170 | 234 |
| 1-Iodobutane | 129 | 184 | 280 |
| 2-Iodobutane | 123 | 184 | 249 |
| 1-Iodo-2-methylpropane | 122 | 184 | 244 |
| 1-Iodopentane | 138 | 198 | 316 |
| Methylene chloride | 94 | 85 | 213 |
| Chloroform | 108 | 119 | 237 |
| Carbon tetrachloride | 120 | 154 | 263 |
| 1,1-Dichloroethane | 103 | 99 | 242 |
| *cis*-1,2-Dichloroethylene | 110 | 97 | 284 |
| 2,3-Dichloropropene | 110 | 111 | 260 |
| Trichloroethylene | 115 | 131 | 265 |
| 1-Bromo-2-chloroethane | 110 | 143 | 224 |
| Dibromomethane | 107 | 174 | 184 |
| Bromochloromethane | 100 | 129 | 188 |
| 1,2-Dibromoethane | 117 | 188 | 216 |
| Fluorobenzene | 105 | 96 | 254 |
| *o*-Fluorotoluene | 116 | 110 | 301 |
| *p*-Fluorotoluene | 117 | 110 | 308 |
| 1-Chloro-3-fluorobenzene | 119 | 131 | 288 |
| Chlorobenzene | 116 | 113 | 294 |
| *o*-Chlorotoluene | 128 | 127 | 342 |
| Benzene | 100 | 78 | 260 |

[a] Data reported by DIETZ[11].

The theory underlying the derivation of this equation has been described else-where[3]. Since irregular trends in diameters appear in the literature, we chose to generate a consistent set of molecular diameters through the empirical equations satisfying the Lennard–Jones (12-6) potential function. Relevant to the present study is the diameter expression

$$\sigma_i = 0.785 \, V_{c_i}^{\frac{1}{3}} \tag{2}$$

which has been developed specifically for polar compounds[7] in conjunction with the 12-6 potential. $V_c$ represents critical volume (ml/gmole). In Table I, the accuracy of our technique is exhibited for selected polar compounds.

A unique feature of the $RMR$ equation is that the critical volume of a substance may be estimated if its $RMR$ value with the TC cell is known. Critical volumes, especially important to theoreticians, are experimentally obtained only with an elaborate apparatus and with great difficulty. Although the critical properties of hydrocarbons have been well characterized[8], critical volume data for polar substances are extremely scarce. In general, no reliable estimation methods have been suggested. One reason for this is that there is a shortage of good experimental values upon which to base an estimating procedure[9]. For halogenates and nitrogen-containing compounds, in particular, there is a definite need for a reliable estimating process.

The critical volumes of the compounds listed in Table I have been experimentally determined; thus, since these volumes accurately reproduce the $RMR$ data, a path is established for the estimation of $V_c$ for other similar polar species. After substitution of eqn. 2 into eqn. 1, the $RMR$ equation may then be rearranged to yield

$$V_{c_i} = \left[ \frac{RMR \times B}{100 \times A} - V_{c_i}^{\frac{1}{3}} \right]^3 \tag{3}$$

where

$$A = \left[ \frac{M_i - M_1}{M_\phi - M_1} \right]^{\frac{1}{2}} \quad \text{and} \quad B = [V_{c_\phi}^{\frac{1}{3}} + V_{c_i}^{\frac{1}{3}}]^2$$

The critical volumes of helium and benzene are 57.8 and 260 ml/gmole, respectively. Insertion of these values simplifies eqn. 3 to

$$V_{c_i} = \left[ \frac{1.05 \, RMR}{A} - 3.86 \right]^3 \tag{4}$$

Once the $RMR$ value of a substance is known, its $V_c$ may be approximated by eqn. 4. In Table II, a detailed tabulation of estimated critical volumes is shown for numerous polar compounds whose critical volumes have not been heretofore measured or cannot be estimated by other procedures[10].

We suggest that the utilization of $RMR$ data can rapidly provide an approximate value for an important fundamental molecular property. More significantly,

the lack of $V_c$ data in the literature can be temporarily circumvented until experimental measurements are reported.

*Department of Chemistry, Lowell Technological Institute,*          EUGENE F. BARRY
*Lowell, Mass. 01854 (U.S.A.)*                                       RICHARD TRAKIMAS

*Department of Chemistry, University of Rhode Island,*             DOUGLAS M. ROSIE
*Kingston, R. I. 02881 (U.S.A.)*

1 D. M. ROSIE AND R. L. GROB, *Anal. Chem.*, 29 (1957) 1263.
2 A. E. MESSNER, D. M. ROSIE AND P. A. ARGABRIGHT, *Anal. Chem.*, 31 (1959) 230.
3 E. F. BARRY AND D. M. ROSIE, *J. Chromatogr.*, 59 (1971) 269.
4 E. F. BARRY AND D. M. ROSIE, *J. Chromatogr.*, 63 (1971) 203.
5 E. F. BARRY, R. S. RISCHER AND D. M. ROSIE, *Anal. Chem.*, 44 (1972) 1559.
6 A. B. LITTLEWOOD, *Nature*, 184 (1959) 1631.
7 L. I. STIEL AND G. THODOS, *J. Chem. Eng. Data*, 1 (1962) 234.
8 R. C. REID AND T. R. SHERWOOD, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 2nd ed., 1966, pp. 571–584.
9 R. C. REID AND T.R. SHERWOOD, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 2nd ed., 1966, p. 27.
10 A. L. LYDERSEN, *Coll. Eng., Univ. Wis. Eng. Exp. Stn. Rep.*, 3, Madison, Wisc., April, 1955.
11 W. A. DIETZ, *J. Gas Chromatogr.*, 5 (1971) 68.