



ELSEVIER

Journal of Chromatography A, 721 (1995) 139–145

JOURNAL OF
CHROMATOGRAPHY A

Influence of prediction method of the second virial coefficient on inverse gas chromatographic parameters

Adam Voelkel^{a,*}, Jacek Fall^b

^a*Poznań University of Technology, Institute of Chemical Technology and Engineering, Pl.M.Skłodowskiej-Curie 2, 60-965 Poznań, Poland*

^b*Institute of Petroleum Processing, ul.Lukasiewicza 1, 31-429 Kraków, Poland*

Received 1 June 1995; accepted 12 July 1995

Abstract

Methods of prediction of the second virial coefficient which may be used in calculation of inverse gas chromatographic parameters are presented. It is shown that these predictions led to various B_{11} -values. Moreover, the final result, i.e. Flory–Huggins interaction parameter $\kappa_{1,2}^{\infty}$ and/or mass activity coefficient Ω_1^{∞} is also different. However, the relative differences between inverse gas chromatographic parameter are one order of magnitude lower than those of the second virial coefficient. Variations in inverse gas chromatographic parameters depend also on the stationary phase used.

1. Theory

The number of empirical and semiempirical equations-of-state, which allow to establish existing relationships between the variables p , V and T exceeds 150. Each of them is the result of the theoretical interpretation of a relatively simple model of interactions or represents an empirical relationship valid for a given class of compounds or substances. Individual properties of each class are taken into account by introducing additional factors into the equation which are constant for this group. The Van der Waals equation is most often used for the description of the behaviour of a real gas. It presents a correct qualitative

description of gases and liquids and predicts the existence of a critical point. However, for non-ideal gases – even under relatively low pressure – satisfactory agreement between predicted and experimental data is seldom observed [1]. Therefore, the well-known virial equation of state was proposed to overcome existing difficulties in the description of correlations between p , V and T :

$$pV = RT + Bp + Cp^2 + Dp^3 + \dots \quad (1)$$

For an ideal gas all virial coefficients (B , C , D , ...) are equal to zero. In other words, virial coefficients are the measure of gas non-ideality caused by the presence of bi-, trimolecular etc. interactions in a real gas at a given temperature.

In the examination of polymers and other materials by inverse gas chromatography [2]

* Corresponding author.

knowledge of the solute binary parameter is necessary. This value is used in calculations of:

(i) Flory–Huggins interaction parameter $\kappa_{1,2}^\infty$:

$$\kappa_{12}^\infty = \ln\left(\frac{273.15 R}{P_1^0 V_g M_1}\right) - \frac{P_1^0}{RT} (B_{11} - V_1^0) + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1^0}{V_2^0}\right) \quad (2)$$

where M_1 , P_1^0 , B_{11} , V_1^0 , ρ_1 and V_g^0 are the molecular mass, saturated vapour pressure, second virial coefficient, molar volume and specific retention volume of the solute, respectively; ρ_2 and V_2^0 are the density and molar volume of the stationary phase; T is column temperature, and R is the gas constant; $\kappa_{1,2}^\infty$ was further used in prediction of the solubility parameter of polymers and their mixtures [2].

(ii) Mass activity coefficient Ω_1^∞

$$\ln \Omega_1^\infty = \ln\left(\frac{a_1}{w_1}\right) = \ln\left(\frac{273.15 R}{P_1^0 V_g M_1}\right) - \frac{P_1^0}{RT} (B_{11} - V_1^0) \quad (3)$$

where a_1 is the activity coefficient and w_1 is the mass of a solute.

(iii) Partial molar free energy of solution ΔG_1^∞ :

$$\Delta G_1^\infty = RT \ln \Omega_1^\infty \quad (4)$$

Condor and Young [3] indicated that “there are no really satisfactory results for predicting second virial coefficient of polar substances although it is possible to extend the principle of corresponding states to substances with small dipole moments with limited success”. They have stated also that the permissible uncertainty in estimation of second virial coefficient of solute should be $\pm 10\%$ (at 20–50°C).

Several methods which are most often used in prediction of second virial coefficient are presented below. According to the principle of corresponding states [4,5] for any two gases two relationships are valid

$$\frac{B_{11}}{V_{11}^c} = \Phi\left(\frac{T}{T_{11}^c}\right) \quad (5)$$

and

$$\frac{B_{22}}{V_{22}^c} = \Phi\left(\frac{T}{T_{22}^c}\right) \quad (6)$$

where V_{11}^c , T_{11}^c , V_{22}^c and T_{22}^c are the critical volumes and temperatures of species 1 and 2, respectively, while Φ is the same function function for both gases. Applications of Eqs. (5) and (6) lead Guggenheim and McGlashan [6] to the following relationship

$$\frac{B_{11}}{V^c} = 0.461 - 1.158\left(\frac{T^c}{T}\right) - 0.503\left(\frac{T^c}{T}\right)^3 \quad (7)$$

where B_{11} is expressed in cm^3/mol , V^c in ml/g , T and T^c in K (valid for Eqs. 7–10). This relationship was used, e.g. by Martire in his work on theoretical aspects of gas chromatography [7].

McGlashan and Wormald [8] corrected Eq. 7 by introducing an extra term

$$\frac{B_{11}}{V^c} = 0.430 - 0.886\left(\frac{T^c}{T}\right) - 0.694\left(\frac{T^c}{T}\right)^2 - 0.0375(n-1)\left(\frac{T^c}{T}\right)^{4.5} \quad (8)$$

where n is the number of carbon atoms in hydrocarbons.

Guggenheim and Wormald [9] applied another version of Eq. 7

$$\frac{B_{11}}{V^c} = 0.500 - 1.144\left(\frac{T^c}{T}\right) - 0.480\left(\frac{T^c}{T}\right)^2 - 0.042\left(\frac{T^c}{T}\right)^3 \quad (9)$$

while for paraffinic hydrocarbons having 1 to 8 carbon atoms they proposed to calculate B_{11} from

$$\frac{B_{11}}{V^c} = 0.0375(n-1)\left(\frac{T^c}{T}\right)^{4.5} \quad (10)$$

Blu et al. [10] and Nesterov and Lipatov [11] predicted B_{11} values from

$$B_{11} = \frac{9RT^c}{128p^c} \left\{1 - 6\left(\frac{T^c}{T}\right)^2\right\} \quad (11)$$

The authors proposed to calculate the second virial coefficient from the relatively simple relationship

$$B_{11} = V_c[0.25 - 1.5(T^c/T)] \quad (12)$$

in the case when $0.6 > T/T^c < 1.0$.

Pitzer and Curl [12] and O'Connell and Prausnitz [13] introduced the acentric factor (ω_i) – a measure of deviations from the properties of a simple, inert gas. They predicted B_{11} values from general relationship

$$\frac{p^c B_{11}}{RT^c} = f_B^{(0)}(T_R) + \omega_i f_B^{(1)}(T_R) \quad (13)$$

where p^c and T^c denote critical pressure and temperature, respectively; T_R is reduced temperature equal to the ratio T/T_c ; ω_i is defined as

$$\omega_i \equiv -\lg(p_i^s/p^c) - 1.000 \quad (14)$$

where p_i^s is the saturated vapour pressure when $T/T_c = 0.7$; factors $f_B^{(0)}(T_R)$ and $f_B^{(1)}(T_R)$ are calculated from the following equations:

$$f_B^{(0)}(T_R) = 0.1445 - \frac{0.330}{T_R} - \frac{0.1385}{T_R^2} - \frac{0.0121}{T_R^3} \quad (15)$$

$$f_B^{(1)}(T_R) = 0.073 + \frac{0.46}{T_R} - \frac{0.50}{T_R^2} - \frac{0.097}{T_R^3} - \frac{0.0073}{T_R^8} \quad (16)$$

Besides these two factors these authors [13] introduced also the unit: $f_u(\mu_R, T_R)$ and presented values of ω_H (acentric factor) and μ (dipole moment) for the series of gases consisting of polar, organic molecules.

To calculate the second virial coefficient from Eqs. 7–10 and 12 knowledge of the critical pressure is not necessary. The critical pressure may be also calculated from the general relationship [14] valid for all molecules

$$p^c = \frac{20.8 T^c}{V^c - 8} \quad (17)$$

and the error of prediction does not exceed 11% (V^c expressed in ml/mol, T^c in K and p^c in atm).

For a mixture of two different chemical substances Cruickshank et al. [15] presented a relationship which allowed to calculate B_{11} :

Table 1

Comparison of second virial coefficient values calculated from various relationships at 373.15 K

Test substance	B_{11} (cm ³ /mol) predicted from					
	Eq. 7	Eq. 8	Eq. 9	Eq. 11	Eq. 13	From Ref. [20]
<i>n</i> -Pentane	-632	-687	-555	-664	-773	-526
<i>n</i> -Hexane	-878	-1011	-747	-932	-1419	-783
<i>n</i> -Heptane	-1168	-1494	-973	-1233	-1514	-1102
<i>n</i> -Octane	-1505	-2085	-1322	-1577	-2086	-1584
<i>n</i> -Nonane	-2049	-	-1428	-1879	-2578	-2093
<i>n</i> -Decane	-2281	-	-1784	-2359	-3576	-2633
Benzene	-	-	-	-821	-1226	-768
Toluene	-	-	-	-1136	-1274	-1077
2-Butanone	-	-	-	-	-1256	-664
1-Nitropropane	-	-	-	-	-894	-
Pyridine	-	-	-	-	-1051	-907
1,4-Dioxane	-	-	-	-	-998	-
<i>m</i> -Cresol	-	-	-	-1547	-3034.6	-
Acetic acid	-	-	-	-611	-969	-

$$\frac{B_{11}}{V_{1,2}^c} = 0.430 - 0.886\left(\frac{T_{1,2}^c}{T}\right) - 0.694\left(\frac{T_{1,2}^c}{T}\right)^2 - 0.0375\left(\frac{n_1 + n_2}{2}\right)\left(\frac{T_{1,2}^c}{T}\right)^{4.5} \quad (18)$$

where $V_{1,2}^c$ and $T_{1,2}^c$ are pseudocritical volume and temperature, respectively; n_1 and n_2 denote the number of carbon atoms in two hydrocarbons constituting the mixture. The most widely applicable rules for calculation of $V_{1,2}^c$ and $T_{1,2}^c$ were discussed by Conder and Young [16]. Please, do check the formal similarity of Eqs. 8 and 18. McGlashan and Potter [17] predicted B_{11} for binary mixture from the following relationship

$$B_{11} = (1-x)^2 V_A^c \Phi(T_A^c/T) + 2(1-x)V_{AB}^c \Phi(T_{AB}^c/T) + x^2 V_B^c \Phi(T_B^c/T) \quad (19)$$

where V_{AB}^c and T_{AB}^c are pseudocritical volume and temperature calculated from

$$V_{AB}^c = [(V_A^c)^{1/3} + (V_B^c)^{1/3}]^3 / 8 \quad (20)$$

$$T_{AB}^c = (T_A^c T_B^c)^{1/2} \quad (21)$$

and Φ is the universal function.

The general method of B_{11} prediction was presented by Hayden and O'Connell [18]. For calculation of the second virial coefficient B_{11} knowledge of the critical parameters and temperature of the experiment is required. The second virial coefficient is also tabulated for a rather limited group of compounds in several handbooks, e.g. [19].

Inverse gas chromatographic applications

The point of interest is if the accuracy of prediction of the binary parameter significantly affect the resulting values of the physicochemical parameters used in characterization of polymers and their mixtures. The values of B_{11} calculated with the use of several relationships presented above at 373.15 K are presented in Table 1.

Additionally, some B_{11} values were found by extrapolation of data presented in Ref. [20]. Values of critical parameters (pressure, volume and temperature) were taken from Refs. [21–24].

The values of the second virial coefficient for selected test solutes differ significantly. Differences very often exceed the 10% limit indicated by Conder and Young as the accepted limit of uncertainty. The highest relative variation of B_{11} expressed as $((B_{11\max} - B_{11\min})/B_{11\min}) \times 100\%$ was found for *n*-hexane (90%), *n*-decane (100%) and *m*-cresol (96.2%) (Fig. 1A). Most often the values for the relative variation exceed

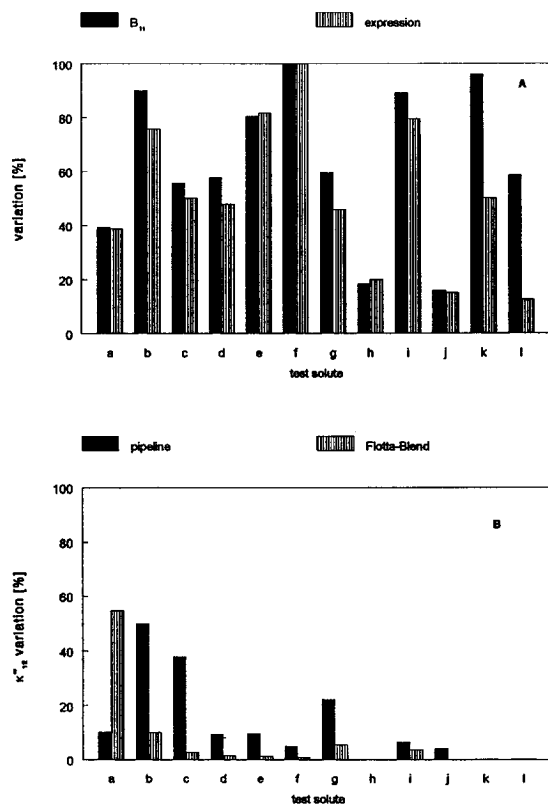


Fig. 1. Variation of second virial coefficient B_{11} , expression $-(p_1^0/RT)(B_{11} - V_1^0)$ from Eq. 2 (A) and Flory-Huggins interaction parameter $\kappa_{1,2}^{\infty}$ calculated with the use of various B_{11} values for two stationary phases (pipeline and Flotta-Blend petroleum residues as in Tables 2 and 3) (B); a = *n*-pentane; b = *n*-hexane; c = *n*-heptane; d = *n*-octane; e = *n*-nonane; f = *n*-decane; g = benzene; h = toluene; i = 2-butanone; j = pyridine; k = *m*-cresol; l = acetic acid.

50% and only for benzene and pyridine rather low values were found, i.e. 18.3 and 15.9%, respectively. These variations in B_{11} significantly influence the following values of the expression $-(p_1^0/RT)(B_{11} - V_1^0)$ (see Table 2). The relative variations calculated in the same way as for the second virial coefficient are also significant (Fig. 1A). For *n*-alkanes these variations are almost the same as those for B_{11} and the expression $-(p_1^0/RT)(B_{11} - V_1^0)$. Although the values for the latter expression decrease with increasing molar mass as well as with decreasing saturated vapour pressure of the solute, the observed differences do not follow this rule.

The expression $-(p_1^0/RT)(B_{11} - V_1^0)$ is further used in Eq. 2 to calculate the Flory–Huggins interaction parameter $\kappa_{1,2}^\infty$ and/or in Eq. 3 to give the mass activity coefficient Ω_1^∞ . Therefore, one may expect that the values of both physicochemical parameters will also depend on changes in the second virial coefficient values. In fact, Flory–Huggins interaction parameter $\kappa_{1,2}^\infty$ -values tabulated in Table 3 differ when using B_{11} predicted by different methods. The values of $\kappa_{1,2}^\infty$ were calculated with the use of retention data collected for comparable fractions from two petroleum fractions used as liquid stationary

phases in chromatographic column. These fractions were obtained in a separation process of vacuum residues from pipeline oil and Flotta–Blend oil.

The relative variations in $\kappa_{1,2}^\infty$ calculated as for B_{11} were much lower than those of the second virial coefficient and the expression $-(p_1^0/RT)(B_{11} - V_1^0)$ (Fig. 1B). Generally, they did not exceed 10%, and only in some cases were higher, e.g. for *n*-pentane (Flotta–Blend pitch) (54.7%) or *n*-hexane (pipeline oil pitch) (50%) (Table 1). It is also clear that the range of variation was affected by the stationary phase used in gas chromatographic experiment. The $\kappa_{1,2}^\infty$ variation parameter for Flotta–Blend oil residue fraction is significantly lower than for the corresponding fraction from pipeline oil residue.

The Flory–Huggins interaction parameter $\kappa_{1,2}^\infty$ is often discussed as the measure of mutual solubility for solute–polymer systems. We have shown that the significant variations in second virial coefficient data possibly collected from different sources affect the final result, i.e. the physicochemical parameters which are used for discussion of the practical application of polymer and petroleum systems. The variations in the resulting data do not change the selection of a

Table 2
Comparison of expression $-(p_1^0/RT)(B_{11} - V_1^0)$ calculated for various B_{11} values at 373.15 K

Test substance	$-(p_1^0/RT)(B_{11} - V_1^0)$ expression for B_{11} value calculated from					
	Eq. 7	Eq. 8	Eq. 9	Eq. 11	Eq. 13	From Ref. [20]
<i>n</i> -Pentane	0.166	0.178	0.149	0.173	0.176	0.143
<i>n</i> -Hexane	0.080	0.091	0.070	0.084	0.123	0.072
<i>n</i> -Heptane	0.040	0.056	0.038	0.047	0.057	0.043
<i>n</i> -Octane	0.026	0.034	0.023	0.027	0.034	0.027
<i>n</i> -Nonane	0.016	–	0.011	0.015	0.020	0.016
<i>n</i> -Decane	0.008	–	0.006	0.008	0.012	0.009
Benzene	–	–	–	0.059	0.086	0.056
Toluene	–	–	–	0.005	0.006	0.005
2-Butanone	–	–	–	–	0.079	0.044
1-Nitropropane	–	–	–	–	0.030	–
Pyridine	–	–	–	–	0.023	0.020
1,4-Dioxane	–	–	–	–	0.035	–
<i>m</i> -Cresol	–	–	–	0.001	0.002	–
Acetic acid	–	–	–	0.016	0.018	–

Table 3
Comparison of Flory–Huggins interaction parameter $\kappa_{1,2}^{\infty}$ calculated for various B_{11} values at 373.15 K

Test substance	$\kappa_{1,2}^{\infty}$ parameter calculated for B_{11} value predicted from					
	Eq. 7	Eq. 8	Eq. 9	Eq. 11	Eq. 13	From Ref. [20]
<i>The aromatic fraction Ar II ($1.53 < n_D^{20} < 1.55$) separated from pipeline petroleum residue used as stationary phase [25]</i>						
<i>n</i> -Pentane	-0.562	-0.574	-0.545	-0.569	-0.594	-0.539
<i>n</i> -Hexane	-0.116	-0.127	-0.106	-0.120	-0.159	-0.108
<i>n</i> -Heptane	0.067	0.051	0.069	0.060	0.050	0.064
<i>n</i> -Octane	0.125	0.117	0.128	0.124	0.117	0.124
<i>n</i> -Nonane	0.098	–	0.103	0.099	0.094	0.098
<i>n</i> -Decane	0.124	–	0.126	0.124	0.120	0.123
Benzene	–	–	–	-0.137	-0.164	-0.134
Toluene	–	–	–	1.726	1.725	1.726
2-Butanone	–	–	–	–	0.540	0.575
1-Nitropropane	–	–	–	–	1.797	–
Pyridine	–	–	–	–	-0.077	-0.074
1,4-Dioxane	–	–	–	–	0.276	–
<i>m</i> -Cresol	–	–	–	0.920	0.919	–
Acetic acid	–	–	–	1.295	1.293	–
<i>The aromatic fraction Ar II ($1.53 < n_D^{20} < 1.55$) separated from Flotta–Blend petroleum residue used as stationary phase [25]</i>						
<i>n</i> -Pentane	0.065	0.053	0.082	0.058	0.053	0.088
<i>n</i> -Hexane	0.569	0.558	0.579	0.565	0.526	0.577
<i>n</i> -Heptane	0.728	0.712	0.730	0.721	0.711	0.725
<i>n</i> -Octane	0.763	0.755	0.766	0.762	0.755	0.762
<i>n</i> -Nonane	0.769	–	0.774	0.770	0.765	0.769
<i>n</i> -Decane	0.768	–	0.770	0.768	0.764	0.767
Benzene	–	–	–	0.549	0.522	0.552
Toluene	–	–	–	2.343	2.342	2.343
2-Butanone	–	–	–	–	0.937	0.972
1-Nitropropane	–	–	–	–	2.482	–
Pyridine	–	–	–	–	^a	^a
1,4-Dioxane	–	–	–	–	0.779	–
<i>m</i> -Cresol	–	–	–	1.767	1.766	–
Acetic acid	–	–	–	2.035	2.033	–

^a Retention data not obtained because of adsorption of the solute into the stationary phase.

given solute as good or poor solvent for the examined liquid phase. However, one should take into account the possible error of estimation caused by the uncertainty in the physicochemical data which may, in several cases, exceed 10% of the value of the inverse gas chromatographic parameter.

Acknowledgement

Authors thank Dr. K. Alejski for his friendly discussions during preparation of this paper.

References

- [1] N.A. Smirnova, in *Methods of Statistical Thermodynamic in Physical Chemistry*, PWN, Warsaw, 1980, p. 299, (in Polish).
- [2] A. Voelkel, *Crit. Rev. Anal. Chem.*, 22 (1991) 411.
- [3] J.R. Conder and C.L. Young, in *Physicochemical Measurements by Gas Chromatography*, Wiley & Sons, Chichester, 1979, p. 334.
- [4] K.S. Pitzer, *J. Chem. Phys.*, 7 (1939) 253.
- [5] E.A. Guggenheim, *J. Chem. Phys.*, 13 (1945) 253.
- [6] E.A. Guggenheim and M.L. McGlashan, *Proc. Roy. Soc. A*, 206 (1951) 448.
- [7] D.E. Martire, *Anal. Chem.*, 38 (1966) 244.

- [8] M.L. McGlashan and C.J. Wormald, *Trans. Faraday Soc.*, 60 (1964) 646.
- [9] E.A. Guggenheim and C.J. Wormald, *J. Chem. Phys.*, 42 (1965) 3775.
- [10] G. Blu, L. Jacob and G. Guiochon, *J. Chromatogr.*, 50 (1970) 1.
- [11] A.E. Nesterov and J.S. Lipatov, *Obrascenna Gazovaja Khromatografija v Termodinamike Polimerov*, Naukovaja Dumka, Kiev, 1976, p. 13.
- [12] K.S. Pitzer and R.F. Curl Jr., *J. Am. Chem. Soc.*, 79 (1957) 2369.
- [13] J.P. O'Connell and J.M. Prausnitz, *Ind. Eng. Chem., Prod. Res. Dev.*, 6 (1967) 245.
- [14] *Spravocnik Khimika*, G.N.T., Izd. Khim. Lit., Leningrad, 1962, p. 917.
- [15] A.J.B. Cruickshank, M.L. Windsor and C.L. Young, *Proc. Royal Soc.*, 295 (1966) 286.
- [16] J.R. Conder and C.L. Young, in *Physicochemical Measurements by Gas Chromatography*, Wiley & Sons, Chichester, 1979, pp. 336–338.
- [17] M.L. McGlashan and D.J.B. Potter, *Proc. Roy. Soc. A*, 267 (1962) 478.
- [18] J.G. Hayden and J.P. O'Connell, *Ind. Eng. Chem., Proc. Des. Dev.*, 14 (1975) 209.
- [19] J.H. Dymond and E.B. Smith, *The Virial Coefficients of Pure Gases and Mixtures*, Clarendon Press, Oxford, 1980.
- [20] A. Voelkel and J. Janas, *J. Chromatogr.*, 645 (1993) 141.
- [21] T.E. Jordan, *Vapor Pressure of Organic Compounds*, Interscience Publishers, New York, London, 1954.
- [22] R.R. Dreisbach, *Physical Properties of Chemical Compounds*, Vol. III, 22, *Am. Chem. Soc.*, 1955.
- [23] R.R. Dreisbach, *Physical Properties of Chemical Compounds*, Vol. III, 29, *Am. Chem. Soc.*, 1955.
- [24] D.R. Stull, E.F. Westrum Jr. and G.C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, J. Wiley & Sons, London, 1969.
- [25] J. Fall and A. Voelkel, to be published.