

CHROM. 15,469

## THERMOCHEMICAL INVESTIGATIONS OF GAS-LIQUID CHROMATOGRAPHY

### II. PARTITION COEFFICIENTS OF ALCOHOL SOLUTES ON BINARY SOLVENT MIXTURES OF INERT HYDROCARBONS

WILLIAM E. ACREE, Jr.

*Department of Chemistry, Kent State University, Kent, OH 44242 (U.S.A.)*

(Received September 15th, 1982)

---

#### SUMMARY

An expression is derived for the chromatographic behavior of alcohol solutes on binary solvent mixtures of inert hydrocarbons based on the Kretschmer–Wiebe and Mecke–Kempter association models. The expression predicts a logarithmic relationship between the partition coefficient of the solute,  $K_{R(BC)}$ , and solvent composition,  $\varphi_B$ :

$$\ln K_{R(BC)} = \varphi_B \ln K_{R(B)}^0 + \varphi_C \ln K_{R(C)}^0 + \frac{\bar{V}_A \Delta \bar{G}_{BC}^{th}}{(X_B \bar{V}_B + X_C \bar{V}_C) RT}$$

and is identical with an expression derived earlier for systems containing only non-specific interactions. The fact that the above expression can be derived for both inert and self-associating solutes suggests that it is impossible to determine a solute's mode of self-association through chromatographic measurements on binary solvent mixtures.

---

#### INTRODUCTION

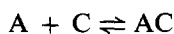
It is now well established that reliable thermodynamic data for volatile solutes at infinite dilution in non-volatile solvents can be obtained using gas-liquid chromatography (GLC). Indeed, for such Henry's-law-region investigations, the GLC method is preferred over classical static vapor pressure methods because of the speed and ease with which data can be obtained for a wide variety of solutes. Moreover, inter-laboratory comparisons of GLC measurements and extrapolated static vapor data have clearly demonstrated that infinite dilution solute activity coefficients,  $\gamma_A^\infty$ , accurate to better than  $\pm 1\%$  are currently attainable from GLC. This finding is particularly encouraging as precise thermodynamic data are needed in testing theories of non-electrolyte mixtures.

The nearly ideal binary solvent model (NIBS), developed by Bertrand and co-

workers, has been shown to be dependable for estimating heats of solution<sup>1,2</sup>, solubilities<sup>3-7</sup> and gas-liquid partition coefficients<sup>8,9</sup> in binary solvent systems that are free of association. The predictive equation for the chromatographic partition coefficient,  $K_{R(BC)}$ ,

$$\ln K_{R(BC)} = \varphi_B \ln K_{R(B)}^0 + \varphi_C \ln K_{R(C)}^0 + \frac{\bar{V}_A \Delta \bar{G}_{BC}^{th}}{(X_B \bar{V}_B + X_C \bar{V}_C) RT} \quad (1)$$

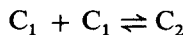
requires only *a priori* knowledge of the solute's partition coefficients on the two pure solvents [ $K_{R(B)}^0$  and  $K_{R(C)}^0$ ] and the solvent's volume fraction composition ( $\varphi_B$ ) and excess Gibbs free energy of mixing ( $\Delta \bar{G}_{BC}^{th}$ ) relative to the Flory-Huggins model. Extensions of the basic NIBS approach to more complex systems led to the development of equations for partition coefficients in systems containing solute-solvent complexation<sup>9</sup>:



$$K_{AC} = \frac{\varphi_{AC}}{\varphi_A \varphi_C}$$

$$\begin{aligned} \ln K_{R(BC)} = & \varphi_B \ln K_{R(B)}^0 + \varphi_C \ln K_{R(C)}^0 - \varphi_C \ln [1 + K_{AC} \bar{V}_A / \bar{V}_{AC}] + \\ & \ln [1 + K_{AC} \varphi_C \bar{V}_A / \bar{V}_{AC}] + \frac{\bar{V}_A \Delta \bar{G}_{BC}^{th}}{(X_B \bar{V}_B + X_C \bar{V}_C) RT} \end{aligned} \quad (2)$$

or a dimerizable solvent component<sup>10</sup>:



$$K_D = \frac{\varphi_{C_2}}{\varphi_{C_1} \varphi_{C_1}}$$

$$\ln K_{R(BC)} = \varphi_B \ln K_{R(B)}^0 + \varphi_C \ln K_{R(C)}^0 + \frac{\bar{V}_A (\varphi_{C_1} - \varphi_C \varphi_{C_1}^0)}{2 \bar{V}_C} + \frac{\bar{V}_A \varphi_B \varphi_C A_{BC_1}}{RT} \quad (3)$$

where  $\varphi_{C_1}$  and  $\varphi_{C_1}^0$  refer to the monomeric concentration of component C in the binary mixture and pure C, respectively,  $\bar{V}_i$  is the molar volume of a pure liquid, and  $A_{BC_1}$  is a binary interaction parameter for the B + C solvent system.

Although eqns. 1-3 do permit one to describe the chromatographic behavior of a large number of ternary systems, there still remains the question of how self-associating solutes should be treated. As an answer to this question, this paper presents the development of predictive expressions for alcohol solutes based on the Kreschmer-Wiebe<sup>11</sup> and Mecke-Kempter<sup>12</sup> association models.

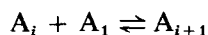
#### KRETSCHMER-WIEBE ASSOCIATION MODEL

Generally the development of a solution model begins by assuming that the

Gibbs free energy of mixing can be described by the sum of two separate contributions, one contribution representing chemical interactions and the other representing physical interactions:

$$\Delta G_{ABC}^{\text{mix}} = (\Delta G_{ABC}^{\text{mix}})_{\text{chem}} + (\Delta G_{ABC}^{\text{mix}})_{\text{phys}} \quad (4)$$

The chemical contribution  $(\Delta G_{ABC}^{\text{mix}})_{\text{chem}}$  is based on the associated solution theory proposed by Kretschmer and Wiebe, which assumes that the alcohol (component A) forms continuous linear hydrogen-bonded polymers  $A_1, A_2, \dots, A_n$  by successive chemical reactions:



with a single isodesmic equilibrium constant of the form

$$K_A = \frac{\varphi_{A_{i+1}}}{\varphi_{A_i}\varphi_{A_1}} \cdot \frac{i}{i+1} = \frac{C_{A_{i+1}}}{C_{A_i}C_{A_1}}$$

where  $C_{A_i}$  and  $\varphi_{A_i}$  refer to the molar concentration and volume fraction of the  $i$ -mer, respectively, calculated using the molar volume of the monomer ( $\bar{V}_A$ ) multiplied by  $i$ . The stoichiometric volume fraction of alcohol ( $\varphi_A$ ) is related to the volume fractions of each individual alcohol species:

$$\varphi_A = \sum_{i=1}^{\infty} \varphi_{A_i} = (1/K_A) \sum_{i=1}^{\infty} i (K_A \varphi_{A_1})^i = \varphi_{A_1} (1 - K_A \varphi_{A_1})^{-2} \quad (5)$$

It should be noted that  $K_A \varphi_{A_1}$  must be less than one for the infinite series to converge.

The chemical part of the Gibbs free energy is based on the Flory-Huggins athermal model and may be written as

$$(\Delta G_{ABC}^{\text{mix}})_{\text{chem}} = RT \left( \sum_{i=1}^{\infty} n_{A_i} \ln \varphi_{A_i} + n_B \ln \varphi_B + n_C \ln \varphi_C \right) \quad (6)$$

Combining eqn. 6 with a Scatchard-Hildebrand-type expression for the physical interactions:

$$\begin{aligned} (\Delta G_{ABC}^{\text{mix}})_{\text{phys}} = & \left( n_B \bar{V}_B + n_C \bar{V}_C + \sum_{i=1}^{\infty} n_{A_i} \bar{V}_{A_i} \right)^{-1} \\ & \left( n_B \bar{V}_B n_C \bar{V}_C A_{BC} + \sum_{i=1}^{\infty} n_{A_i} \bar{V}_{A_i} n_B \bar{V}_B A_{A_i B} + \sum_{i=1}^{\infty} n_{A_i} \bar{V}_{A_i} n_C \bar{V}_C A_{A_i C} \right) \quad (7) \end{aligned}$$

one writes the total free energy of mixing of the ternary alcohol-two inert hydrocarbons system as

$$\begin{aligned} \Delta G_{ABC}^{\text{mix}} = & RT \left( \sum_{i=1}^{\infty} n_{A_i} \ln \varphi_{A_i} + n_B \ln \varphi_B + n_C \ln \varphi_C \right) + \left( n_B \bar{V}_B + n_C \bar{V}_C + \sum_{i=1}^{\infty} n_{A_i} \bar{V}_{A_i} \right)^{-1} \\ & \left( n_B \bar{V}_B n_C \bar{V}_C A_{BC} + \sum_{i=1}^{\infty} n_{A_i} \bar{V}_{A_i} n_B \bar{V}_B A_{A_i B} + \sum_{i=1}^{\infty} n_{A_i} \bar{V}_{A_i} n_C \bar{V}_C A_{A_i C} \right) \quad (8) \end{aligned}$$

The chemical potentials of the individual components relative to the pure liquids ( $\mu_i^*$ ) are obtained through the appropriate differentiation:

$$\mu_{A_1} - \mu_{A_1}^* = RT \left( \ln \varphi_{A_1} + 1 - \frac{\bar{V}_A}{\bar{V}_{\text{soln}}} \right) + \bar{V}_A \left( \varphi_B A_{A_1B} + \varphi_C A_{A_1C} - \sum_{i=1}^{\infty} \varphi_B \varphi_{A_i} A_{A_1B} - \sum_{i=1}^{\infty} \varphi_C \varphi_{A_i} A_{A_1C} - \varphi_B \varphi_C A_{BC} \right) \quad (9)$$

$$\mu_B - \mu_B^* = RT \left( \ln \varphi_B + 1 - \frac{\bar{V}_B}{\bar{V}_{\text{soln}}} \right) + \bar{V}_B \left[ (1 - \varphi_B) \sum_{i=1}^{\infty} \varphi_{A_i} A_{A_1B} + (1 - \varphi_B) \varphi_C A_{BC} - \sum_{i=1}^{\infty} \varphi_{A_i} \varphi_C A_{A_1C} \right] \quad (10)$$

and

$$\mu_C - \mu_C^* = RT \left( \ln \varphi_C + 1 - \frac{\bar{V}_C}{\bar{V}_{\text{soln}}} \right) + \bar{V}_C \left[ (1 - \varphi_C) \sum_{i=1}^{\infty} \varphi_{A_i} A_{A_1C} + (1 - \varphi_C) \varphi_B A_{BC} - \sum_{i=1}^{\infty} \varphi_B \varphi_{A_i} A_{A_1B} \right] \quad (11)$$

where  $\bar{V}_{\text{soln}}$  is the molar volume of the true solution:

$$\frac{1}{\bar{V}_{\text{soln}}} = \sum_{i=1}^{\infty} \frac{\varphi_{A_i}}{\bar{V}_{A_i}} + \frac{\varphi_B}{\bar{V}_B} + \frac{\varphi_C}{\bar{V}_C}$$

As shown in many thermodynamic textbooks (for example, ref. 13) the chemical potential of stoichiometric component C is equal to the chemical potential of the monomeric species in solution:

$$\mu_C = \mu_{C_1}$$

To obtain the customary excess properties of the solution, pure substance C must be taken as the new reference state:

$$\mu_C - \mu_C^0 = RT \left[ \ln (\varphi_{A_1} / \varphi_{A_1}^0) - \frac{\bar{V}_A}{\bar{V}_{\text{soln}}} + \frac{\bar{V}_A}{\bar{V}_{\text{soln}}^0} \right] + \bar{V}_A \left( \varphi_B A_{A_1B} + \varphi_C A_{A_1C} - \sum_{i=1}^{\infty} \varphi_B \varphi_{A_i} A_{A_1B} - \sum_{i=1}^{\infty} \varphi_C \varphi_{A_i} A_{A_1C} - \varphi_B \varphi_C A_{BC} \right) \quad (12)$$

Combining eqns. 9-12, we write the excess Gibbs free energy as

$$\Delta G_{ABC}^{\text{ex}} = RT [n_A \ln (\varphi_{A_1} / \varphi_{A_1}^0 X_A) + n_B \ln (\varphi_B / X_B) + n_C \ln (\varphi_C / X_C) + n_A K_A (\varphi_{A_1} - \varphi_{A_1}^0)] + (n_A \bar{V}_A + n_B \bar{V}_B + n_C \bar{V}_C)^{-1} (n_A \bar{V}_A n_B \bar{V}_B A_{A_1B} + n_A \bar{V}_A n_C \bar{V}_C A_{A_1C} + n_B \bar{V}_B \bar{V}_C A_{BC}) \quad (13)$$

where

$$X_i = n_i / (n_A + n_B + n_C)$$

and

$$n_A = \sum_{i=1}^{\infty} i n_{A_i}$$

For a system obeying eqn. 13, the activity coefficient of component A at infinite dilution is

$$RT \ln \gamma_{A(BC)}^{\infty} = RT \left\{ \ln \left[ \frac{\bar{V}_A}{(X_B \bar{V}_B + X_C \bar{V}_C) \varphi_{A_1}^0} \right] + 1 - K_A \varphi_{A_1}^0 - \frac{\bar{V}_A \varphi_B}{\bar{V}_B} - \frac{\bar{V}_A \varphi_C}{\bar{V}_C} \right\} + \bar{V}_A [\varphi_B A_{A_1 B} + \varphi_C A_{A_1 C} - \varphi_B \varphi_C A_{BC}] \quad (14)$$

The molar fractions and volume fraction compositions are now calculated as if the solute were not present. The  $A_{A_1 B}$  and  $A_{A_1 C}$  interaction parameters can be eliminated from the model via the infinite dilution activity coefficients in the pure solvents,  $\gamma_{A(B)}^{\infty}$  and  $\gamma_{A(C)}^{\infty}$ :

$$\ln \gamma_{A(BC)}^{\infty} = \varphi_B \ln \gamma_{A(B)}^{\infty} + \varphi_C \ln \gamma_{A(C)}^{\infty} + \ln \left[ \frac{(\bar{V}_B)^{\varphi_B} (\bar{V}_C)^{\varphi_C}}{X_B \bar{V}_B + X_C \bar{V}_C} \right] - \frac{\bar{V}_A \varphi_B \varphi_C A_{BC}}{RT} \quad (15)$$

Gas-liquid partition coefficients are related to activity coefficients through the definition

$$K_R = \frac{RTQ}{P_A^0 \gamma_A^{\infty} \bar{V}_{\text{soln}}}$$

where  $P_A^0$  is the equilibrium vapor pressure of the solute at the specified temperature and  $Q$  is a temperature-dependent term involving the molar volume of the solute and the second virial coefficients of the solute and carrier gas. When this relationship is used, eqn. 15 becomes

$$\ln K_{R(BC)} = \varphi_B \ln K_{R(B)}^0 + \varphi_C \ln K_{R(C)}^0 + \frac{\bar{V}_A \Delta \bar{G}_{BC}^{\text{th}}}{(X_B \bar{V}_B + X_C \bar{V}_C) RT}$$

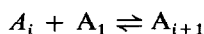
identical with eqn. 1 whenever the Gibbs free energy of the binary solvent pair:

$$\Delta \bar{G}_{BC}^{\text{th}} = (X_B \bar{V}_B + X_C \bar{V}_C) \varphi_B \varphi_C A_{BC}$$

is used to replace the  $A_{BC}$  interaction parameter.

## MECKE-KEMPTER ASSOCIATION MODEL

Although the Kretschmer-Wiebe model is one of the most popular solution models for interpreting the thermodynamic properties of alcohol-hydrocarbon mixtures, it is by no means the only self-association model. Equally popular is the Mecke-Kempter<sup>12</sup> model, which describes the formation of hydrogen-bonded polymers:



with an isodesmic equilibrium constant:

$$K_A = \frac{\varphi_{A_{i+1}}}{\varphi_{A_i}\varphi_{A_1}}$$

expressed in terms of volume fractions rather than molar concentrations (moles/liter). For such a ternary alcohol-two inert hydrocarbons system, it can be shown that the excess Gibbs free energy of mixing is given by

$$\Delta G_{ABC}^{ex} = RT \left[ n_A \ln (\varphi_{A_1}/\varphi_{A_1}^0 X_A) + n_B \ln (\varphi_B/X_B) + n_C \ln (\varphi_C/X_C) - \frac{(n_A \bar{V}_A + n_B \bar{V}_B + n_C \bar{V}_C) \ln (1 + K_A \varphi_A)}{\bar{V}_A K_A} + \frac{n_A \ln (1 + K_A)}{K_A} \right] +$$

$$(n_A \bar{V}_A + n_B \bar{V}_B + n_C \bar{V}_C)^{-1} (n_A \bar{V}_A n_B \bar{V}_B A_{A_1 B} + n_A \bar{V}_A n_C \bar{V}_C A_{A_1 C} + n_B \bar{V}_B n_C \bar{V}_C A_{BC}) \quad (16)$$

with the volume fraction of the alcohol monomer ( $\varphi_{A_1}$ ) calculated from

$$\varphi_{A_1} = \varphi_A / (1 + K_A \varphi_A)$$

the overall alcohol concentration and equilibrium constant. Differentiation of eqn. 16 with respect to the number of moles of component A, followed by suitable mathematical manipulations, yields the following expression for the infinite dilution activity coefficient of the solute:

$$\ln \gamma_{A(BC)}^\infty = \varphi_B \ln \gamma_{A(B)}^\infty + \varphi_C \ln \gamma_{A(C)}^\infty + \ln \frac{(\bar{V}_B^{\varphi_B} \bar{V}_C)^{\varphi_C}}{X_B \bar{V}_B + X_C \bar{V}_C} - \frac{\bar{V}_A \Delta \bar{G}_{BC}^{Th}}{(X_B \bar{V}_B + X_C \bar{V}_C) RT} \quad (17)$$

Expressed in terms of gas-liquid partition coefficients, we find that eqn. 17 is identical with eqn. 1.

## DISCUSSION

During the course of these derivations, several other solution models were

tried, ranging from the simple monomer-dimer, monomer-trimer models, etc., to the more sophisticated two-constant Kretschmer-Wiebe association model (1-2-∞). In every instance, it was possible to re-derive eqn. 1 provided that the non-specific interactions were described with a Scatchard-Hildebrand-type equation. Based on these observations, it is concluded that the self-association characteristics of a solute cannot be deduced by studying its chromatographic behavior.

An important consequence of this work concerns the applicability of eqn. 1 to chromatographic measurements. In deriving eqn. 1 from their nearly ideal binary solvent model, Acree and Bertrand<sup>8</sup> assumed that only non-specific interactions were present. As a result, several workers have tended to criticize eqn. 1 because it was thought to be applicable to very few systems of practical importance. At this time, however, we discover that eqn. 1 can be used to represent the partition coefficients of self-associating solutes on binary solvent mixtures of inert hydrocarbons. Further, through the appropriate differentiation of eqns. 13 and/or 16 it may be possible to predict partition coefficients in systems containing a self-associating solvent component. The subject certainly merits further study.

In conclusion, readers are reminded that there is an important difference between using empirical models and thermodynamic models to describe partition coefficients in binary solvent mixtures. Empirical models limit gas-liquid chromatography to routine analysis and chemical separations. Thermodynamic models, in comparison, also permit the calculation of thermodynamic quantities and encourage the development of future (and hopefully better) solutions models.

#### REFERENCES

- 1 T. E. Burchfield and G. L. Bertrand, *J. Solution Chem.*, 4 (1975) 205.
- 2 T. E. Burchfield, *Ph.D. Dissertation*, University of Missouri-Rolla, 1977.
- 3 W. E. Acree, Jr. and G. L. Bertrand, *J. Phys. Chem.*, 81 (1977) 1170.
- 4 W. E. Acree, Jr. and G. L. Bertrand, *J. Pharm. Sci.*, 70 (1981) 1033.
- 5 W. E. Acree, Jr. and J. H. Rytting, *J. Pharm. Sci.*, 71 (1982) 201.
- 6 W. E. Acree, Jr. and J. H. Rytting, *Int. J. Pharm.*, 10 (1982) 231.
- 7 W. E. Acree, Jr. and J. H. Rytting, *J. Pharm. Sci.*, in press.
- 8 W. E. Acree, Jr. and G. L. Bertrand, *J. Phys. Chem.*, 83 (1979) 2355.
- 9 W. E. Acree, Jr. and J. H. Rytting, *Anal. Chem.*, 52 (1980) 1765.
- 10 W. E. Acree, Jr., *J. Phys. Chem.*, 86 (1982) 1461.
- 11 C. B. Kretschmer and R. Wiebe, *J. Chem. Phys.*, 22 (1954) 1697.
- 12 H. Kempter and R. Mecke, *Z. Phys. Chem. Abt. B*, 46 (1940) 229.
- 13 I. Prigogine and R. Defay, *Chemical Thermodynamics*, Wiley, New York, 1954.