# Vapor-liquid equilibrium for systems that contain more than one alcohol: Comparison of Kretschmer-Wiebe and mobile order models[1]

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**ABSTRACT**

As part of a continuing study of associated mixtures, we compare the abilities of two solution models to represent vapor-liquid equilibria for binary mixtures of alcohols. Specifically, we compare mobile order theory, in which the degree of association is governed by the fraction of time for which a molecule is free of hydrogen bonding, to the Kretschmer-Wiebe model, in which hydrogen bonding is modelled classically by chemical equilibria. Both models contain parameters which reflect physical interactions, self-association and cross-association and both contain the same number of adjustable parameters. In addition to comparing the abilities of each model to represent VLE data, we examine the temperature dependence of the model parameters.

Key Words: alcohols, association, vapor-liquid equilibria

## Introduction

The application of association models to vapor-liquid equilibria of alcohol+hydrocarbon systems has been the topic of numerous studies. However, most work has focused on binary alkane+alcohol systems and less attention has been given to binary alcohol+alcohol systems. One might think that the nearly ideal behavior of these systems does not justify the complication of using an association model to calculate their phase equilibria. However, it must be kept in mind that any association model applied to a system comprised of an arbitrary number of associating and nonassociating species must reduce to the appropriate behavior for each of the constituent binary systems. Therefore, it is important that such models be tested with alcohol+alcohol systems as well as alkane+alcohol systems.

In this work, we compare the abilities of two association models, the Kretschmer-Wiebe model [1,2] and mobile order theory [3-7], to represent vapor-liquid equilibrium of binary alcohol+alcohol systems. In the Kretschmer-Wiebe model, alcohol molecules are assumed to form hydrogen-bonded complexes in solution and the distribution of these complexes is determined by classical chemical equilibria. In mobile order theory, the contribution of hydrogen bonding to the excess Gibbs free energy is expressed in terms of the fraction of time that a given molecule is free of hydrogen bonding.

## Theory

We present here the Kretschmer-Wiebe and mobile order expressions for the excess Gibbs free energy of binary alcohol(A)+alcohol(B) mixture. We assume for both models that the excess Gibbs free energy can be expressed as a sum of contributions due to chemical

and physical effects and that the physical contribution for each is in the form of the Scatchard-Hildebrand regular solution model:

$$\left(\frac{G^E}{RT}\right)_{phys} = \frac{(x_A r_A + x_B r_B)}{RT}\Phi_A \Phi_B \beta_{AB} \tag{1}$$

where $\beta_{AB}$ is a parameter which reflects physical interactions between alcohols A and B. The size parameter $r_i$ of species i (i=A,B) is defined arbitrarily by $r_i = (V_i/V_{MeOH})_{303.15\ K}$ where $V_i$ and $V_{MeOH}$ are saturated liquid volumes of pure liquid i and of methanol, respectively. The volume fraction of a species i (i=A,B) is defined by

$$\Phi_i = \frac{r_i x_i}{r_A x_A + r_B x_B} \tag{2}$$

For mobile order, the chemical contribution to the excess Gibbs free energy [8] is given by:

$$\left(\frac{G^E}{RT}\right)_{chem} = 0.5\left[x_A \ln\left(\frac{\Phi_A}{x_A}\right) + x_B \ln\left(\frac{\Phi_B}{x_B}\right)\right] + x_A \ln\left(\frac{1 + K_{AA}/V_A}{1 + K_{AA}\Phi_A/V_A + K_{AB}\Phi_B/V_B}\right)$$
$$+ x_B \ln\left(\frac{1 + K_{BB}/V_B}{1 + K_{AB}\Phi_A/V_A + K_{BB}\Phi_B/V_B}\right) \tag{3}$$

where $K_{AA}$ and $K_{BB}$ are self-association constants for alcohols A and B and where $K_{AB}$ is a cross-association constant.

For the Kretschmer-Wiebe model, the chemical contribution to $G^E$ may be written [9] as:

$$\left(\frac{G^E}{RT}\right)_{chem} = x_A \ln\left(\frac{\Phi_A}{x_A}\right) + x_B \ln\left(\frac{\Phi_B}{x_B}\right) + x_A \ln\left(\frac{Z_A}{Z^o{}_A}\right)^2 + x_B \ln\left(\frac{Z_B}{Z^o{}_B}\right)^2$$

$$- x_A(Z_A - Z^o{}_A) - x_B(Z_B - Z^o{}_B) \qquad (4)$$

where $Z_A$ and $Z_B$ are found from simultaneous solution of

$$Z_A = 1 / (1 + K_{AA} Z_A \;\; {}_A / r_A + K_{AB} Z_B \;\; {}_B / r_B) \qquad (5)$$

$$Z_B = 1 / (1 + K_{AB} Z_A \;\; {}_A / r_A + K_{BB} Z_B \;\; {}_B / r_B) \qquad (6)$$

and where $K^*_{AA}$, $K^*_{BB}$, and $K^*_{AB}$ are association constants analogous to those described above for mobile order theory. Application of the Kretschmer-Wiebe model to binary alcohol+alcohol mixtures requires an iterative solution for the quantities $Z_A$ and $Z_B$. The quantities $Z^o{}_A$ and $Z^o{}_B$ are obtained by applying equation (5) to pure A and equation (6) to pure B and do not require iteration.

For a binary alcohol(A)+alcohol(B) system, each model contains four adjustable parameters $K^*_{AA}$ (or $K_{AA}$), $K^*_{BB}$ (or $K_{BB}$), $K^*_{AB}$ (or $K_{AB}$) and $\beta_{AB}$. However, the two self-association constants $K^*_{AA}$ and $K^*_{BB}$ (or $K_{AA}$ and $K_{BB}$) are best obtained from VLE data for binary alkane+alcohol systems which contain the alcohols in question. This leaves only the cross-association constant $K^*_{AB}$ (or $K_{AB}$) and the physical parameter $\beta_{AB}$ to be determined for each alcohol+alcohol binary. However, since the values of these two parameters will depend somewhat on the chosen values of the self-association constants, some attention will

be given here to alkane+alcohol systems. Although written above for the case of a binary alcohol+alcohol system, both models may be applied to alkane(A) + alcohol(B) systems simply by setting $K^*_{AA}$ and $K^*_{AB}$ (or $K_{AA}$ and $K_{AB}$) to zero.

**Application to Alkane(A)+Alcohol(B)**

In a previous application [10] of the Kretschmer-Wiebe and mobile order models to alkane+alcohol binary systems, the same enthalpy of hydrogen bonding (assumed constant) was used for both models. Since one of our goals is to examine the temperature dependence of the model parameters, these assumptions should be examined.

To this end, several sets of VLE data for alkane+alcohol systems which covered at least a 50 K range in temperature were compiled. Using Barker's method, in which the sum of the squares of the differences between measured and calculated pressures is minimized, each model was fit to each data set with the results given in Table 1. For mobile order, self-association constants are reported as dimensionless numbers $K'_{BB} = K_{BB}/V_B$. The overall average percent deviations in pressure given at the bottom of the table indicate, consistent with earlier work, that the Kretschmer-Wiebe model provides a better representation. In addition, use of the mobile order model sometimes results in a negative value for the physical parameter $\beta_{AB}$

The self-association constants given for both models in Table 1 were scaled to their values at 303.15 K and were plotted as a function of reciprocal temperature in Figure 1. Several important observations can be made. First, the predicted enthalpy of hydrogen bonding $H^o$ (related to the slopes of the curves shown in Figure 1) is model-dependent and is a function of temperature for both models. However, for both models, $H^o$ appears to be

the same function for each alcohol.

Assuming a linear relation between $H^o$ and temperature results in the following temperature dependence for the alcohol self-association constants:

$$\ln\left(\frac{K}{K_{ref}}\right) = a\left(\frac{1}{T} - \frac{1}{T_{ref}}\right) + b\ln\left(\frac{T}{T_{ref}}\right) \qquad (7)$$

where $K = K^*_{BB}$ or $K'_{BB}$ and where $K_{ref}$ is the self-association constant at a reference temperature $T_{ref.}$ Equation (7) was fitted to the self-association constants shown in Figure 1 with the following results: For mobile order, a=-3987.2 K and b=-17.659, and for Kretschmer-Wiebe, a=-5923.0 K and b=-27.573.

Equation (7) was used to draw the smooth curves shown in Figure 1. It was also used to evaluate $H^o$ at 298.15 K for each model, resulting in a value of -19.1 kJ/mol for the Kretschmer-Wiebe model and -10.6 kJ/mol for the mobile order model. Values reported in the literature for the enthalpy of hydrogen bonding for alcohols generally fall between 20 and 25 kJ/mol.

Size parameters and self-association constants for each alcohol examined here are listed in Table 2. These were obtained from VLE data for alkane+alcohol systems at the temperatures indicated in the table. When applied to alcohol+alcohol systems at other temperatures, the self-association constants are corrected to the new temperature using equation (7).

**Application to Alcohol(A)+Alcohol(B) Systems**

Using previously determined self-association constants, Barker's method was used to

evaluate $K^*_{AB}$ (or $K_{AB}$) and $\beta_{AB}$ for the alcohol+alcohol systems shown in Table 3. Rather than list cross-association constants directly, a cross association parameter $C_{AB}$, defined through

$$K_{AB} = C_{AB} \sqrt{K_{AA} K_{BB}} \qquad (8)$$

is reported. Here $K_{ij}$ is either $K^*_{ij}$ or $K_{ij}$. As Table 3 indicates, both methods provide an excellent representation of vapor-liquid equilibrium for most of the alcohol+alcohol systems. The Kretschmer-Wiebe model is slightly more accurate at the expense of requiring an iterative solution for the monomeric concentrations.

For mixtures in which both alcohols are primary, both models yield values of $C_{AB}$ close to unity, suggesting that the geometric mean assumption for $K_{AB}$ is reasonable for this case. However, for mixtures in which one of the components is a secondary or a tertiary alcohol, deviations from the geometric mean rule may be significant for both models, as is indicated by the last seven systems listed in Table 3. It should be noted also that the mobile order model yielded negative values of the physical parameter $\beta_{AB}$ for two systems containing tertiary alcohols.

Since the enthalpy of hydrogen bonding apparently is alcohol-independent, it is reasonable to suppose that the enthalpy of cross-association would be the same as for self-association. This would predict that $C_{AB}$ is independent of temperature. Values of $C_{AB}$ and $\beta_{AB}$ derived from VLE data for alcohol + 1-decanol systems are plotted for both models as functions of temperature in Figure 2. It is observed that both parameters appear to be largely independent of temperature. Assuming such should allow reasonable estimation of

VLE for alcohol+alcohol systems but would probably not be accurate for the estimation of heats of mixing.

**Conclusions**

The Kretschmer-Wiebe and Mobile Order models provide an adequate representation of vapor-liquid equilibrium both for alkane+alcohol and alcohol+alcohol systems. The Kretschmer-Wiebe model is slightly more accurate but requires, when more than one alcohol is present, an iterative solution for the monomeric concentrations. The models predict different (but apparently alcohol-independent) values for the enthalpy of hydrogen bonding.

For alcohol+alcohol mixtures, there is little dependence of the parameters $C_{AB}$ and $\beta_{AB}$ on temperature and, when both alcohols are primary, the geometric mean rule appears to hold for each model. Application of the mobile order model sometimes results in a negative value for the physical parameter $\beta_{AB}$. This is of no consequence in using the model to represent VLE data but it might prove problematic when attempting to correlate this parameter with other physical properties.

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Table 1. Comparison of Kretschmer-Wiebe and Mobile Order Models for Selected Alkane +Alcohol Systems

| | | Kretschmer-Wiebe | | | Mobile Order | | |
|---|---|---|---|---|---|---|---|
| System(ref) | T(K) | $K^*_{BB}$ | $\beta_{AB}$(J/mol) | % $P^b$ | $^aK'_{BB}$ | $\beta_{AB}$(J/mol) | % $P^b$ |
| n-pentane | 303.15 | 396 | 873.9 | 0.5 | 42.8 | 354.2 | 1.7 |
| + methanol | 372.7 | 44.3 | 956.0 | 1.1 | 12.7 | 160.7 | 2.3 |
| (11, 12) | 397.7 | 20.6 | 944.5 | 0.5 | 8.10 | -0.1 | 1.4 |
| | 422.6 | 10.5 | 903.6 | 0.4 | 5.11 | -120.3 | 1.2 |
| n-pentane | 303.15 | 285 | 537.8 | 0.3 | 30.8 | 291.7 | 1.1 |
| + ethanol | 372.7 | 34.5 | 612.6 | 0.4 | 8.85 | 198.0 | 0.3 |
| (11, 13) | 397.7 | 14.9 | 766.6 | 1.0 | 5.31 | 261.1 | 0.8 |
| | 422.6 | 8.99 | 726.3 | 0.6 | 3.75 | 175.5 | 0.3 |
| n-heptane | 303.15 | 176 | 319.7 | 0.3 | 17.4 | 189.3 | 0.8 |
| + 1-butanol | 333.15 | 81.0 | 324.7 | 0.1 | 11.0 | 156.8 | 0.4 |
| (10, 14) | 363.15 | 33.0 | 366.0 | 0.1 | 6.57 | 138.6 | 0.4 |
| n-hexane | 283.16 | 237 | 226.5 | 0.4 | 13.18 | 163.4 | 0.7 |
| + 1-decanol | 303.15 | 141 | 242.8 | 0.3 | 9.71 | 167.9 | 0.6 |
| (15) | 323.15 | 93.5 | 252.9 | 0.1 | 7.61 | 166.2 | 0.4 |
| | 333.15 | 69.8 | 264.9 | 0.1 | 6.34 | 171.4 | 0.4 |
| Overall Average Percent Deviation (201 data points) | | | | 0.4 | | | 0.9 |

[a] $K'_{BB} = K_{BB}/V_B$

[b] average percent deviation in pressure

Table 2. Size Parameters r and Self-Association Constants[a] K' or $K^*$ at Reference Temperature $T_{ref}$ for Alcohols

| Alcohol | r | $T_{ref}$(K) | $K^*$ | K' |
|---|---|---|---|---|
| methanol | 1.00 | 303.15 | 396 | 42.8 |
| ethanol | 1.44 | 303.15 | 285 | 30.8 |
| 1-propanol | 1.85 | 303.15 | 236 | 24.4 |
| 2-propanol | 1.89 | 303.15 | 148 | 19.3 |
| 1-butanol | 2.26 | 303.15 | 176 | 17.4 |
| 2-methyl-1-propanol | 2.28 | 303.15 | 107 | 13.4 |
| 2-butanol | 2.27 | 303.15 | 69.0 | 10.1 |
| 2-methyl-2-propanol | 2.34 | 313.15 | 51.3 | 8.55 |
| 1-pentanol | 2.67 | 313.15 | 120 | 12.7 |
| 2-pentanol | 2.69 | 313.15 | 56.6 | 8.03 |
| 3-pentanol | 2.66 | 313.15 | 43.0 | 6.82 |
| 2-methyl-1-butanol | 2.66 | 313.15 | 87.5 | 10.6 |
| 2-methyl-2-butanol | 2.69 | 313.15 | 44.4 | 7.02 |
| 3-methyl-1-butanol | 2.68 | 313.15 | 109 | 11.9 |
| 3-methyl-2-butanol | 2.66 | 313.15 | 57.4 | 8.12 |
| 1-decanol | 4.70 | 303.15 | 141 | 9.71 |

[a] K' = K/V for mobile order model

Table 3. Application of Kretschmer-Wiebe and Mobile Order Models to Alcohol + Alcohol Systems

| System (ref) | T(K) | Kretschmer-Wiebe $C_{AB}$ | Kretschmer-Wiebe $\beta_{AB}$(J/mol) | Kretschmer-Wiebe % P | Mobile Order $C_{AB}$ | Mobile Order $\beta_{AB}$(J/mol) | Mobile Order % P |
|---|---|---|---|---|---|---|---|
| methanol+ ethanol(11) | 303.15 | 1.04 | 120.3 | 0.06 | 1.04 | 91.4 | 0.05 |
| methanol + 1-propanol(16) | 333.17 | 1.01 | 130.0 | 0.13 | 1.02 | 5.9 | 0.13 |
| methanol + 1-butanol(17) | 298.15 | 1.02 | 304.6 | 0.22 | 1.04 | 103.0 | 0.21 |
| methanol + 2-methyl-1-propanol(17) | 298.15 | 1.02 | 198.7 | 0.14 | 1.04 | 51.3 | 0.18 |
| methanol + 1-pentanol(18) | 313.15 | 1.01 | 391.7 | 0.07 | 1.05 | 127.4 | 0.08 |
| methanol + 2-methyl-1-butanol(18) | 313.15 | 1.05 | 399.6 | 0.05 | 1.07 | 127.0 | 0.13 |
| methanol + 3-methyl-1-butanol(18) | 313.15 | 1.02 | 349.2 | 0.13 | 1.05 | 79.8 | 0.09 |
| methanol + decanol(19) | 293.15 | 0.90 | 829.4 | 0.33 | 1.00 | 316.5 | 0.49 |
| | 303.15 | 0.89 | 798.7 | 0.44 | 1.00 | 295.9 | 0.54 |
| | 313.15 | 0.90 | 819.3 | 0.26 | 1.00 | 274.9 | 0.56 |
| | 323.15 | 0.90 | 819.2 | 0.28 | 1.00 | 251.3 | 0.57 |
| ethanol + 1-propanol(20) | 303.15 | 1.04 | 159.3 | 0.07 | 1.03 | 113.1 | 0.06 |
| ethanol + 2-methyl-1-propanol(21) | 303.15 | 1.07 | 249.4 | 0.19 | 1.05 | 167.1 | 0.19 |
| ethanol + 1-decanol(19) | 293.15 | 0.97 | 354.0 | 0.14 | 1.02 | 111.2 | 0.27 |
| | 303.15 | 0.96 | 332.0 | 0.07 | 1.02 | 87.4 | 0.24 |
| | 313.15 | 0.96 | 327.3 | 0.07 | 1.02 | 74.6 | 0.26 |
| | 323.15 | 0.97 | 343.0 | 0.15 | 1.04 | 85.3 | 0.33 |
| 1-propanol + 1-decanol(22) | 293.15 | 0.99 | 214.6 | 0.24 | 1.03 | 104.6 | 0.30 |
| | 303.15 | 0.98 | 204.4 | 0.17 | 1.03 | 92.3 | 0.33 |
| | 313.15 | 0.98 | 201.8 | 0.12 | 1.03 | 84.2 | 0.27 |
| | 323.15 | 0.99 | 201.7 | 0.10 | 1.03 | 71.0 | 0.22 |
| methanol + 2-butanol(17) | 298.15 | 1.21 | 320.8 | 0.25 | 1.15 | 10.2 | 0.08 |
| methanol + 2-pentanol(18) | 313.15 | 1.17 | 363.5 | 0.08 | 1.16 | 52.6 | 0.22 |
| methanol + 3-pentanol(18) | 313.15 | 1.24 | 392.0 | 0.10 | 1.20 | 60.1 | 0.32 |
| methanol + 3-methyl-2-butanol(18) | 313.15 | 1.20 | 347.9 | 0.12 | 1.19 | 40.2 | 0.20 |
| ethanol + 2-propanol(20) | 303.15 | 1.06 | 92.0 | 0.04 | 1.05 | 39.6 | 0.04 |
| methanol + 2-methyl-2-propanol(17) | 298.15 | 1.35 | 121.2 | 0.11 | 1.29 | -207.2 | 0.35 |
| methanol + 2-methyl-2-butanol(18) | 313.15 | 1.34 | 177.6 | 0.63 | 1.28 | -190.0 | 1.02 |
| Overall Average Percent Deviation (475 data points) | | | | 0.16 | | | 0.26 |

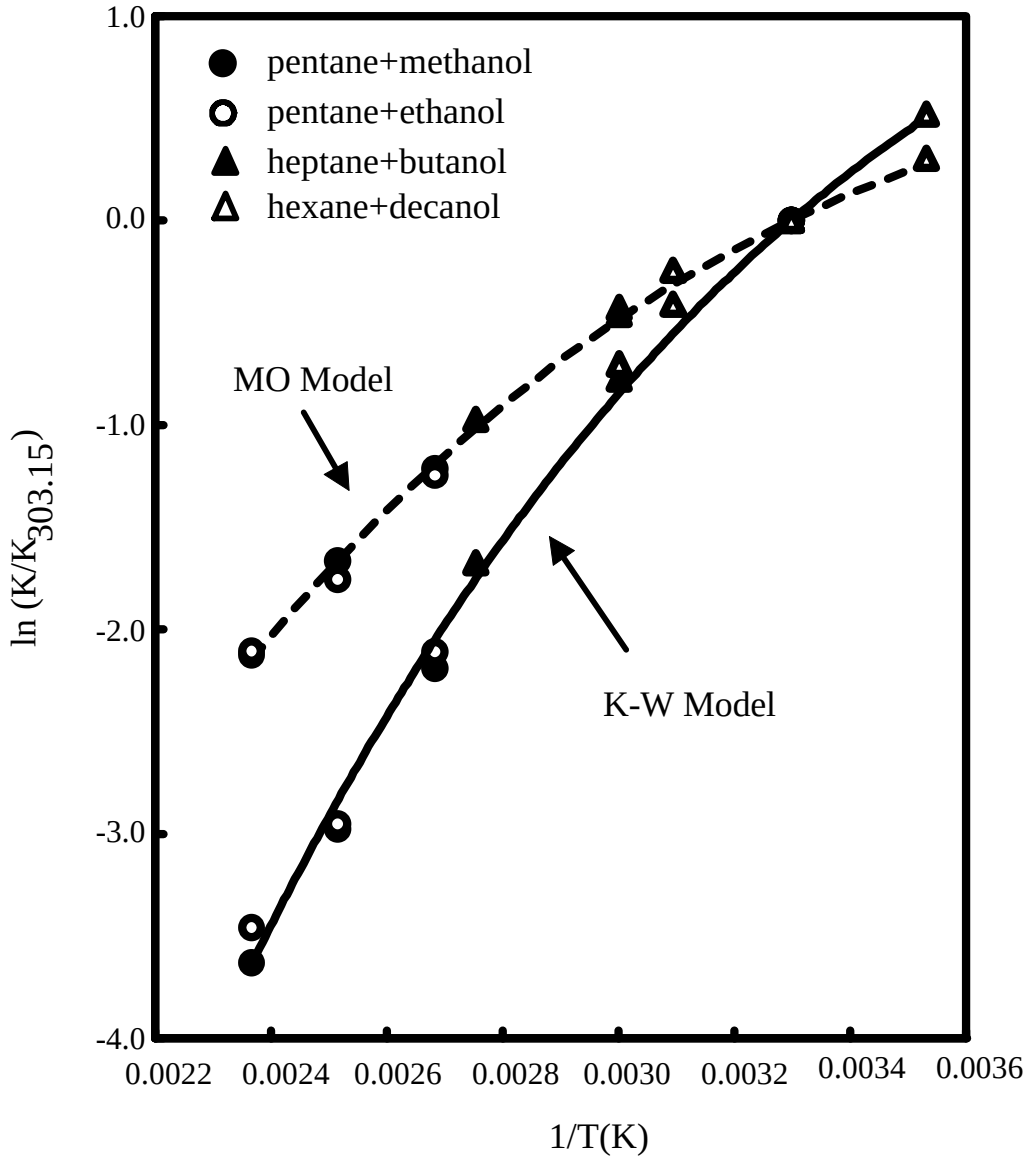


Figure 1. Dependence of Self-Association Constants K on Temperature T for Kretschmer-Wiebe and Mobile Order Models (K is K' for Mobile Order and $K^*$ for Kretschmer-Wiebe)

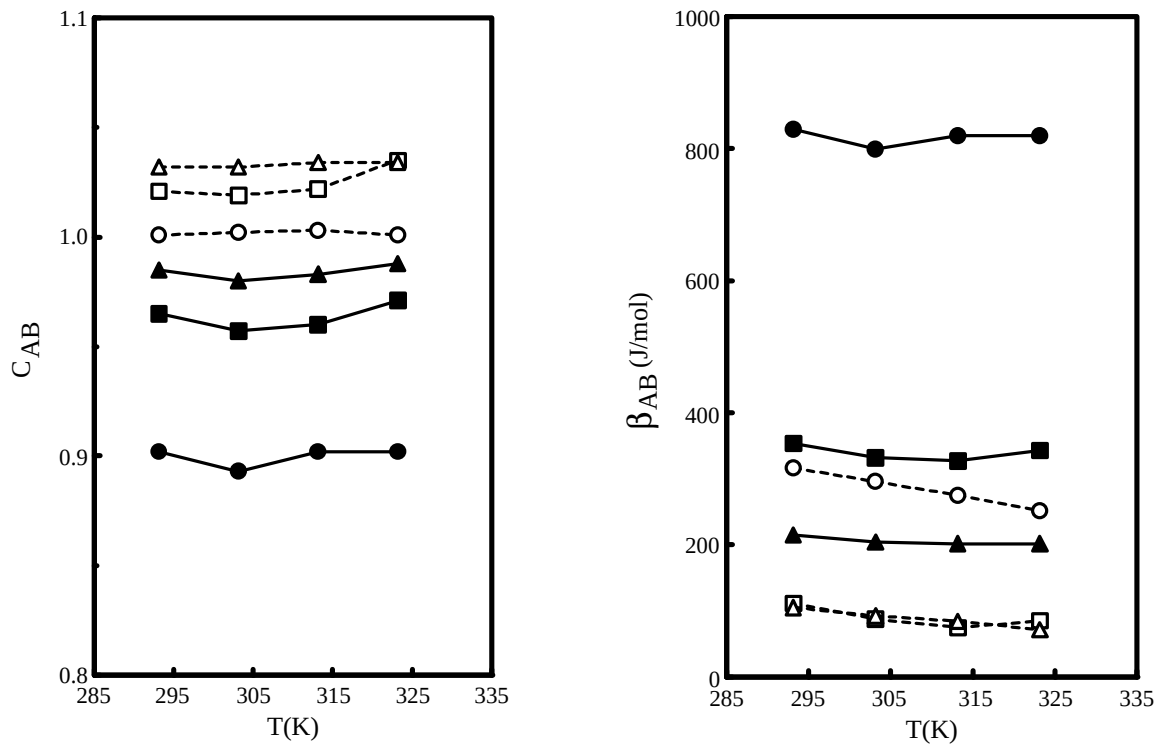


Figure 2. Temperature Dependence of Cross Association Parameter $C_{AB}$ and Physical Parameter $\$_{AB}$ for Kretschmer-Wiebe (solid lines) and Mobile Order (dashed lines) Models. (Circles are methanol + 1-decanol, squares are ethanol + 1-decanol and triangles are 1-propanol + 1-decanol)