Thermodynamics of Ternary Alcohol -Hydrocarbon Mixtures

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Thermodynamics of Ternary Alcohol-Hydrocarbon Mixtures

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With 3 Figures and 7 Tables

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Abstract

The original Kretschmer-Wiebe equation which is applicable to only binary alcohol-saturated hydrocarbon solutions is extended to ternary alcohol-unsaturated hydrocarbon mixtures. Prediction of vapor-liquid equilibrium data is shown to be successful for 14 ternary alcohol-hydrocarbon systems and 4 ternary hydrocarbon systems from only binary parameters. Predicted heat of mixing data are compared with experimental results for the ethanol-benzene-cyclohexane system at 25°C. The capability of the theory is also demonstrated for binary systems alcohols with methyl acetate, ethyl acetate ethyl ether, acetone.

Introduction

Flory's theory of mixtures of polymers was applied to solutions of alcohols and saturated hydrocarbons by KRETSCHMER and WIEBE [1] and later RENON and PRAUSNITZ [2] gave a critical discussion of the theory by reducing excess Gibbs energy data and enthalpy of mixing data for binary alcohol-saturated hydrocarbon solutions. The main feature of the theory involves that alcohol is self-associated and interacts with hydrocarbon only by physical forces. The theory gives a good representation of the experimental data. RENON and PRAUSNITZ stated that the association model can be extended to mixtures of alcohols with aromatic hydrocarbons or carbon tetrachloride by taking into consideration formation of complexes between alcohol and solvent molecules as briefly suggested by KRETSCHMER and WIEBE. CHEN-SHOW-AN [3] derived such an equation and stated that the modified Kretschmer-Wiebe equation was physically incorrect. His claim was based on the observation that the equilibrium constant between alcohol *i*-mer and hydrocarbon determined from the excess Gibbs free energy data of the ethanol-toluene mixture was found to increase with increasing temperature. The present author [4] demonstrated that the model is still effective in a simultaneous fit of the excess Gibbs free energy data and excess enthalpy of mixing data for 5 alcohol-aromatic hydrocarbon systems and 4 alcohol-carbon tetrachloride systems.

WIEBE et al. [5] coupled the two-parameter Flory-Huggins equation with stoichiometric models of alcohol association and interaction with nonassociating solvents to obtain a quantitative description of the activity coefficients and heats of mixing of these solutions. Their equations for the activity coefficients are considerably complicated. Their approach is based upon that proposed by WIEBE and BAGLEY [6]. KEHIAIAN [7] pointed out that the Wiebe-Bagley model is not consistent, but the Kretschmer-Wiebe model is consistent. In this investigation the modified Kretschmer-Wiebe equation for binary alcohol-

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unsaturated hydrocarbon solutions is extended to ternary alcohol-hydrocarbon mixtures to examine the capability of the association model. It is also used for binary alcohol mixtures with methyl acetate, ethyl acetate, ethyl ether, and acetone.

Derivation of Equations

1) Excess Gibbs Free Energy

The basic assumptions of the association model are summarized below. A refers to alcohol, B and C represent hydrocarbons.

[1] The alcohol polymerizes linearly and at the same time the alcohol and the hydrocarbon form alcohol-hydrocarbon complexes according to successive chemical reactions expressed by

[2] The volume change on mixing is zero. That is, the volumes of alcohol i -mer, and of alcohol-hydrocarbon complexes, A_iB and A_iC , are, respectively, iV_A , $iV_A + V_B$ and $iV_A + V_C$.

[3] The association constants of the chemical reactions are independent of i .

[4] Both the chemical and physical contributions are responsible for the deviation of alcohol-hydrocarbon solutions from an ideal solution.

We suppose that a ternary alcohol mixture consists of n_i moles of alcohol i -mer, n_{iB} moles of alcohol-hydrocarbon complex A_iB and n_{iC} moles of alcohol-hydrocarbon complex A_iC . The total number of moles of chemical species is represented by

$$N = \sum_{i=1}^{\infty} n_i + \sum_{i=0}^{\infty} n_{iB} + \sum_{i=0}^{\infty} n_{iC} \quad (1)$$

One stoichiometric mole of the alcohol hydrocarbon solution contains x_a moles of alcohol, x_b moles of hydrocarbon B and x_c moles of hydrocarbon C . The overall mole fraction of each component is given in terms of the mole number of chemical species.

$$x_a = \sum_{i=1}^{\infty} i n_i + \sum_{i=1}^{\infty} i n_{iB} + \sum_{i=1}^{\infty} i n_{iC} \quad (2)$$

$$x_b = \sum_{i=0}^{\infty} n_{iB} \quad (3)$$

$$x_c = \sum_{i=0}^{\infty} n_{iC} \quad (4)$$

The Gibbs free energy of mixing per stoichiometric mole fraction may be written by

$$g^M = RT \left[\sum_{i=1}^{\infty} n_i \ln \phi_i + \sum_{i=0}^{\infty} n_{iB} \ln \phi_{iB} + \sum_{i=0}^{\infty} n_{iC} \ln \phi_{iC} \right] \\ + V_m (\beta_{ab} \phi_a \phi_b + \beta_{ac} \phi_a \phi_c + \beta_{bc} \phi_b \phi_c) \quad (5)$$

$$V_m = x_a V_A + x_b V_B + x_c V_C, \quad (6)$$

where ϕ , V , β , and V_m are, respectively, the volume fraction, the molar volume, the physical interaction parameter, and the volume of one stoichiometric mole of the solution. The chemical potentials of alcohol i -mer and of alcohol-hydrocarbon complexes, are given by differentiating eqn. (5) with respect to the number of moles of each chemical species.

$$\begin{aligned}\mu_i - \mu_i^0 &= RT \left(\ln \phi_i + 1 - \frac{V_i}{V} \right) \\ &\quad + V_A [\beta_{ab}(\phi_b^2 + \phi_b \phi_c) + \beta_{ac}(\phi_b \phi_c + \phi_c^2) - \beta_{bc} \phi_b \phi_c]\end{aligned}\quad (7)$$

$$\begin{aligned}\mu_{iB} - \mu_{iB}^0 &= RT \left(\ln \phi_{iB} + 1 - \frac{V_{iB}}{V} \right) \\ &\quad + V_B [\beta_{bc}(\phi_c^2 + \phi_c \phi_a) + \beta_{ab}(\phi_c \phi_a + \phi_a^2) - \beta_{ac} \phi_c \phi_a]\end{aligned}\quad (8)$$

$$\begin{aligned}\mu_{iC} - \mu_{iC}^0 &= RT \left(\ln \phi_{iC} + 1 - \frac{V_{iC}}{V} \right) \\ &\quad + V_C [\beta_{ac}(\phi_a^2 + \phi_a \phi_b) + \beta_{bc}(\phi_a \phi_b + \phi_b^2) - \beta_{ab} \phi_a \phi_b]\end{aligned}\quad (9)$$

The superscript 0 represents the property of pure component. V is the volume of one true mole of solution.

$$\frac{1}{V} = \sum_{i=1}^{\infty} \frac{\phi_i}{V_i} + \sum_{i=0}^{\infty} \frac{\phi_{iB}}{V_{iB}} + \sum_{i=0}^{\infty} \frac{\phi_{iC}}{V_{iC}} \quad (10)$$

The chemical potential of stoichiometric component is equal to that of the monomer in the associated solution as shown by PRIGOGINE and DEFAY [8].

$$\mu_a = \mu_1 \quad (11)$$

$$\mu_b = \mu_{0B} \quad (12)$$

$$\mu_c = \mu_{0C} \quad (13)$$

From eqns. (7), (8) and (9) we obtain

$$\begin{aligned}\mu_1 &= \mu_1^0 + RT \left(\ln \phi_1 + 1 - \frac{V_A}{V} \right) \\ &\quad + V_A [\beta_{ab}(\phi_b^2 + \phi_b \phi_c) + \beta_{ac}(\phi_b \phi_c + \phi_c^2) - \beta_{bc} \phi_b \phi_c]\end{aligned}\quad (14)$$

$$\begin{aligned}\mu_{0B} &= \mu_{0B}^0 + RT \left(\ln \phi_{0B} + 1 - \frac{V_{0B}}{V} \right) \\ &\quad + V_B [\beta_{bc}(\phi_c^2 + \phi_c \phi_a) + \beta_{ab}(\phi_c \phi_a + \phi_a^2) - \beta_{ac} \phi_c \phi_a]\end{aligned}\quad (15)$$

$$\begin{aligned}\mu_{0C} &= \mu_{0C}^0 + RT \left(\ln \phi_{0C} + 1 - \frac{V_{0C}}{V} \right) \\ &\quad + V_C [\beta_{ac}(\phi_a^2 + \phi_a \phi_b) + \beta_{bc}(\phi_a \phi_b + \phi_b^2) - \beta_{ab} \phi_a \phi_b]\end{aligned}\quad (16)$$

We combine eqns. (11) and (14) to get

$$\begin{aligned}\mu_a = \mu_1^0 + RT \left(\ln \phi_1 + 1 - \frac{V_A}{V} \right) \\ + V_A [\beta_{ab}(\phi_b^2 + \phi_b \phi_c) + \beta_{ac}(\phi_b \phi_c + \phi_c^2) - \beta_{bc} \phi_b \phi_c]\end{aligned}\quad (17)$$

For pure alcohol eqn. (17) becomes

$$\mu_a^0 = \mu_1^0 + RT \left(\ln \phi_1^0 + 1 - \frac{V_A}{V^0} \right) \quad (18)$$

Subtraction of eqn. (18) from eqn. (17) yields

$$\begin{aligned}\mu_a = \mu_a^0 + RT \left(\ln \frac{\phi_i}{\phi_i^0} + \frac{V_A}{V^0} - \frac{V_A}{V} \right) \\ + V_A [\beta_{ab}(\phi_b^2 + \phi_b \phi_c) + \beta_{ac}(\phi_b \phi_c + \phi_c^2) - \beta_{bc} \phi_b \phi_c]\end{aligned}\quad (19)$$

The excess Gibbs free energy of the alcohol-hydrocarbon solution and the activity coefficients of three components are expressed by

$$\begin{aligned}g^E = RT \left(x_a \ln \frac{\phi_1}{\phi_1^0 x_a} + x_b \ln \frac{\phi_{0B}}{x_b} + x_c \ln \frac{\phi_{0C}}{x_c} - \frac{V_m}{V} + \frac{x_a V_A}{V^0} \right) \\ + V_m (\beta_{ab} \phi_a \phi_b + \beta_{ac} \phi_a \phi_c + \beta_{bc} \phi_b \phi_c)\end{aligned}\quad (20)$$

$$\begin{aligned}\ln \gamma_a = \ln \frac{\phi_1}{\phi_1^0 x_a} + \frac{V_A}{V^0} - \frac{V_A}{V} + \frac{V_A}{RT} \\ \times [\beta_{ab}(\phi_b^2 + \phi_b \phi_c) + \beta_{ac}(\phi_b \phi_c + \phi_c^2) - \beta_{bc} \phi_b \phi_c]\end{aligned}\quad (21)$$

$$\begin{aligned}\ln \gamma_b = \ln \frac{\phi_{0B}}{x_b} + 1 - \frac{V_B}{V} + \frac{V_B}{RT} \\ \times [\beta_{bc}(\phi_c^2 + \phi_c \phi_a) + \beta_{ab}(\phi_c \phi_a + \phi_a^2) - \beta_{ac} \phi_c \phi_a]\end{aligned}\quad (22)$$

$$\begin{aligned}\ln \gamma_c = \ln \frac{\phi_{0C}}{x_c} + 1 - \frac{V_C}{V} + \frac{V_C}{RT} \\ \times [\beta_{ac}(\phi_a^2 + \phi_a \phi_b) + \beta_{bc}(\phi_a \phi_b + \phi_b^2) - \beta_{ab} \phi_a \phi_b]\end{aligned}\quad (23)$$

Substituting hydrocarbon for alcohol, we may derive the corresponding equations of multicomponent hydrocarbon mixtures [9].

We define the following chemical equilibrium constants of forming alcohol *i*-mer and alcohol-hydrocarbon complexes.

$$K_A = \frac{C_{i+1}}{C_i C_1 V_A} = \frac{\phi_{i+1}}{\phi_i \phi_1} \frac{i}{i+1} \quad (24)$$

$$K_{AB} = \frac{C_{iB}}{C_i C_{0B} V_A} = \frac{\phi_i}{\phi_i \phi_{0B}} \frac{i \varrho_{AB}}{i + \varrho_{AB}} \quad (25)$$

$$K_{AC} = \frac{C_{iC}}{C_i C_{0C} V_A} = \frac{\phi_i}{\phi_i \phi_{0C}} \frac{i \varrho_{AC}}{i + \varrho_{AC}} \quad (26)$$

where C stands for concentration and ϱ is the ratio of the molar volume of hydrocarbon to that of alcohol.

The stoichiometric volume fractions of three components are related with those of alcohol i -mer and alcohol-hydrocarbon complexes as follows.

$$\phi_a = \sum_{i=1}^{\infty} \phi_i + \sum_{i=1}^{\infty} \frac{V_i n_{ib}}{V} + \sum_{i=1}^{\infty} \frac{V_i n_{ic}}{V} = \frac{\phi_1}{(1 - K_A \phi_1)^2} \left(1 + \frac{K_{AB} \phi_{0B}}{\varrho_{AB}} + \frac{K_{AC} \phi_{0C}}{\varrho_{AC}} \right) \quad (27)$$

$$\phi_b = \sum_{i=0}^{\infty} \frac{V_i n_{ib}}{V} = \phi_{0B} \left[1 + \frac{K_{AB} \phi_1}{(1 - K_A \phi_1)} \right] \quad (28)$$

$$\phi_c = \sum_{i=0}^{\infty} \frac{V_i n_{ic}}{V} = \phi_{0C} \left[1 + \frac{K_{AC} \phi_1}{(1 - K_A \phi_1)} \right] \quad (29)$$

From eqns. (27) to (29) we may get ϕ_1 , ϕ_{0B} , and ϕ_{0C} if the chemical equilibrium constants and the stoichiometric volume fractions of components are given. Then,

$$\frac{1}{V} = \frac{\phi_1}{V_A(1 - K_A \phi_1)} + \frac{\phi_{0B}}{V_B} \left[1 + \frac{K_{AB} \phi_1}{(1 - K_A \phi_1)} \right] + \frac{\phi_{0C}}{V_C} \left[1 + \frac{K_{AC} \phi_1}{(1 - K_A \phi_1)} \right] \quad (30)$$

For pure alcohol V^0 and ϕ_1^0 are given by

$$\frac{1}{V^0} = \frac{1 - K_A \phi_1^0}{V_A} \quad (31)$$

$$\phi_1^0 = \frac{2K_A + 1 - \sqrt{1 + 4K_A}}{2K_A^2} \quad (32)$$

The temperature dependence of the chemical equilibrium constant is expressed by the van't Hoff relation

$$\frac{d \ln K}{d(1/T)} = -\frac{h}{R} \quad (33)$$

where h is the enthalpy of formation of a hydrogen bond and R is the gas constant.

2) Heats of Mixing

The enthalpy of the mixture per mole is given by

$$h_M = h_A \sum_{i=1}^{\infty} (i-1)(n_i + n_{iB} + n_{iC}) + h_{AB} \sum_{i=1}^{\infty} n_{iB} + h_{AC} \sum_{i=1}^{\infty} n_{iC} + h_p^E \quad (34)$$

$$h_p^E = V_m(\beta'_{ab}\phi_a\phi_b + \beta'_{ac}\phi_a\phi_c + \beta'_{bc}\phi_b\phi_c) \quad (35)$$

where $\beta' = \beta - T \frac{d\beta}{dT}$ (36)

The excess molar enthalpy is defined by

$$h^E = h_M - h_M^0 x_a = h_A K_A x_a (\phi_1 - \phi_1^0) + \frac{h_{AB} K_{AB} \phi_{0B} x_a (1 - K_A \phi_1)}{\rho_{AB} \left[1 + \frac{K_{AB} \phi_{0B}}{\rho_{AB}} \right] + \frac{K_{AC} \phi_{0C}}{\rho_{AC}}} + \frac{h_{AC} K_{AC} \phi_{0C} x_a (1 - K_A \phi_1)}{\rho_{AC} \left[1 + \frac{K_{AC} \phi_{0C}}{\rho_{AC}} \right] + \frac{K_{AB} \phi_{0B}}{\rho_{AB}}} + h_p^E \quad (37)$$

where h_M^0 is the value of h_M for pure alcohol.

We present some results derived from the model, which were not described in the previous paper [4]. Figures 1 and 2 show calculated chemical contributions to the excess Gibbs free energy and to the excess enthalpy for $K_A = 100$ and $K_A = 500$, and for the molar volume ratio $\rho = V_B/V_A = 1$ or 2. An increase in K_{AB} decreases the excess Gibbs free energy (Fig. 1). Figure 2 represents how the excess enthalpy is strongly

Fig. 1. g_c^E/RT vs. alcohol mole fraction diagrams

— $K_{AB}/K_A = 0$

- - $K_{AB}/K_A = 0.08$

A. $K_A = 100, \rho = 1$ B. $K_A = 100, \rho = 2$

C. $K_A = 500, \rho = 1$ D. $K_A = 500, \rho = 2$

Fig. 2. h_c^E/h_A vs. alcohol mole fractions diagrams— $K_{AB}/K_A = 0$ --- $K_{AB}/K_A = 0.08, h_{AB}/h_A = 0.2$ - - - $K_{AB}/K_A = 0.08, h_{AB}/h_A = 0.4$ - · - · $K_{AB}/K_A = 0.08, h_{AB}/h_A = 0.6$ A. $K_A = 100, q = 1$ B. $K_A = 100, q = 2$ C. $K_A = 500, q = 1$ D. $K_A = 500, q = 2$

dependent upon the values of K_{AB} and h_{AB}/h_A . We may also reproduce an enthalpy-composition diagram showing both endo- and exothermic regions by taking the proper values of K_{AB} and h_{AB}/h_A into account.

Calculated Results

1) Excess Gibbs Free Energy

For each alcohol we used for K_A and h_A the values given in Table 1 as proposed by RENON and PRAUSNITZ [2] and NAGATA [4]. For binary alcohol-hydrocarbon and alcohol-carbon tetrachloride mixtures K_{AB} and h_{AB} are listed in Table 2. Data reduction for binary systems is presented in Table 3. The table also includes results for hydrocarbon—hydrocarbon and hydrocarbon—carbon tetrachloride mixtures. Having fixed the chemical equilibrium constants, we may obtain β and β' from fitting the experimental excess properties. Least square fitting computer programs were used to obtain β and β' . These values of β and β' were determined by minimizing the sum of squares of the

absolute error in the excess properties. β is generally the temperature-dependent physical interaction parameter; however, since sufficient isothermal vapor—liquid equilibrium data are not always available to estimate the temperature dependence of β for isobaric systems, we assumed that β is independent of temperature for an isobaric system

Table 1. Values of constants for pure alcohols

Alcohol	K_A at 50°C	h_A (kcal/mol)	Ref.
Methanol	450	-6.0	[2]
Ethanol	190	-6.0	[2]
n-Propanol	90	-6.0	[2]
Isopropanol	60	-6.0	[2]
n-Butanol	80	-6.0	[4]

Table 2. Values of constants for alcohol-hydrocarbon and alcohol-carbon tetrachloride mixtures [4]

System	K_{AB} at 25°C	h_{AB} (kcal/mol)
Methanol-benzene	9.5	-2.20
Ethanol-benzene	7.5	-2.20
n-Propanol-benzene	7.0	-2.20
Isopropanol-benzene	6.5	-2.20
n-Butanol-benzene	6.7	-2.20
Methanol-toluene	9.0	-2.20
Ethanol-toluene	7.2	-2.20
n-Propanol-toluene	6.6	-2.20
Isopropanol-toluene	6.3	-2.20
n-Butanol-toluene	6.6	-2.20
Methanol-carbon tetrachloride	2.2	-3.80
Ethanol-carbon tetrachloride	2.0	-3.80
n-Propanol-carbon tetrachloride	2.0	-3.80
Isopropanol-carbon tetrachloride	2.0	-3.80
n-Butanol-carbon tetrachloride	2.0	-3.80

under consideration. In vapor—liquid equilibrium calculations vapor phase non-ideality was taken into consideration. We may calculate the total pressure P and vapor phase mole fraction y by using the following equations

$$P = \sum_{i=1}^{\infty} \frac{\gamma_i x_i f_i^0}{\psi_i} \quad (38)$$

$$y_i = \frac{\gamma_i x_i f_i^0}{P \psi_i} \quad (39)$$

$$f_i^0 = \psi_i^s P_i^s \exp \left[\frac{v_i^L (P - P_i^s)}{RT} \right] \quad (40)$$

Table 3. Calculated results for vapor-liquid equilibrium data of binary systems

System	Temp. or press.	No. of data points	Arith. mean dev.		β (cal/cc)	Ref.
			$ \Delta y $ ($\times 10^3$)	$ \Delta P $ (Torr)		
Benzene-cyclohexane	39-99°C	7	4.4	0.6	3.059	[10]
	50°C	5	10.0	3.9	3.493	[11]
	69-98°C	7	3.4	0.9	2.666	[10]
	70°C	7	8.2	1.8	2.305	[12]
	300 Torr	5	7.1	3.3	3.240	[11]
	760 Torr	5	3.1	1.0	2.367	[11]
	760 Torr	30	2.6	1.4	2.476	[13]
	760 Torr	12	2.0	1.0	2.603	[14]
Benzene-n-heptane	75°C	11	3.3	3.0	2.888	[15]
	180 Torr	9	3.4	1.4	3.831	[16]
	400 Torr	9	4.0	1.4	3.399	[16]
	760 Torr	36	1.5	2.7	2.648	[17]
	760 Torr	18	2.4	1.6	2.856	[18]
Carbon tetrachloride-benzene	40°C	8	4.4	0.9	1.115	[19]
	70°C	8	3.4	1.5	1.080	[19]
Cyclohexane-n-heptane	760 Torr	25	3.7	1.5	0.492	[20]
Cyclohexane-toluene	50°C	5	4.4	1.6	1.941	[21]
	760 Torr	31	3.8	4.3	1.803	[22]
Ethanol-benzene	50°C	5	2.3	1.1	3.626	[11]
	180 Torr	10	8.7	1.2	3.248	[16]
	300 Torr	5	6.2	1.1	3.326	[11]
	400 Torr	10	13.2	2.9	3.114	[16]
	760 Torr	9	7.3	7.7	3.299	[23]
Ethanol-cyclohexane	760 Torr	5	13.8	3.7	2.664	[11]
	50°C	5	5.9	2.0	2.969	[21]
	50°C	5	14.3	6.0	3.037	[11]
	300 Torr	5	14.4	4.7	3.040	[11]
	760 Torr	5	11.4	3.8	2.607	[11]
Ethanol-n-heptane	180 Torr	18	35.7	5.6	3.072	[24]
	400 Torr	18	25.2	11.9	2.134	[24]
	750 Torr	18	32.3	26.0	1.604	[24]
Ethanol-n-hexane	760 Torr	9	18.5	14.2	1.602	[25]
Ethanol-methylcyclopentane	760 Torr	13	13.5	12.4	2.591	[26]
Ethanol-toluene	50°C	5	16.7	3.5	2.297	[21]
n-Hexane-benzene	760 Torr	36	2.0	1.8	3.102	[17]
n-Hexane-methylcyclopentane	760 Torr	29	3.7	0.5	0.221	[17]
Isopropanol-benzene	760 Torr	19	6.1	4.0	4.162	[27]
Isopropanol-cyclohexane	760 Torr	12	10.6	6.7	1.926	[28]
Methanol-benzene	35°C	9	21.2	5.6	3.279	[29]
	55°C	9	13.2	9.3	3.114	[29]
Methanol-carbon tetrachloride	35°C	9	10.7	3.1	2.587	[29]
	55°C	6	13.7	15.7	2.107	[30]
Methylcyclopentane-benzene	760 Torr	33	1.6	1.5	2.550	[22]
n-Propanol-benzene	75°C	13	6.3	2.9	3.562	[15]
n-Propanol-n-heptane	75°C	15	23.0	10.2	1.432	[15]

where f_i^0 , P_i^s , ψ_i , ψ_i^s , and v_i^L are, respectively, the fugacity of pure liquid i at the system temperature and P_i^s , the vapor pressure of pure component i , the fugacity coefficient of component i , the fugacity coefficient of pure component i at the system temperature and P_i^s and the saturated liquid molar volume of pure liquid i .

ψ may be calculated from the virial equation of state truncated after the second virial coefficient term [31]

$$\ln \psi_i = \frac{2}{v} \sum_{j=1}^N y_j B_{ij} - \ln z \quad (41)$$

The compressibility factor z is expressed by

$$z = 1 + \frac{\sum_{i=1}^N \sum_{j=1}^N y_i y_j B_{ij}}{v} \quad (42)$$

where v is the molar volume of vapor mixture and B_{ij} is the second virial coefficient which was obtained using the empirical correlation of O'CONNELL and PRAUSNITZ [32]. A six constant equation and the Antoine equation were used to represent the pure component vapor pressure data [31, 33]. The liquid molar volumes at three different temperatures for each pure component were fitted to a quadratic equation of temperature for interpolation. The critical constants and molar volumes were obtained from the literature [31, 34].

The results of data reduction indicates that the theory described here gives a good representation of the experimental excess Gibbs free energy data. Although equilibrium data for a binary system in question have been often reported by several investigators, equilibrium data for a ternary system and its component binary systems were taken from the same literature whenever possible. Table 4 shows the absolute arithmetic mean deviations of predicted values from experimental total pressure and vapor mole fractions for 18 ternary systems using the parameters given in Table 1. The magnitudes of the deviations indicate that the predicted results are in excellent agreement with the experimental data.

2) Heats of Mixing

To test the present theory only one set of ternary experimental heat of mixing data is available at 25°C for the ethanol—benzene—cyclohexane mixture [42]. The values of parameter and the absolute arithmetic mean deviation of calculated from experimental results for three binary systems are shown in Table 5. Figure 3 illustrates the experimental and calculated data for the systems. The calculated results are in good agreement with the experimental data for the ethanol—cyclohexane [43] and the cyclohexane—benzene mixtures [44]. However, discrepancies between the calculated and observed data become large at low alcohol concentration for the ethanol—benzene system [45]. For the ternary system the deviations of calculated from experimental data become large at lower alcohol and higher benzene concentrations. The absolute arithmetic mean deviation in heats of mixing is 13.8 cal/mol for 18 ternary

Table 4. Predicted results for vapor-liquid equilibrium data of ternary systems

System	Temp. or press.	No. of data points	Arith. mean dev.		Ref.
			$ \Delta y $ ($\times 10^3$)	$ \Delta P $ (Torr)	
Benzene	70°C	21	8	6.7	[12]
n-Hexane			6		
Cyclohexane			5		
Benzene	760 Torr	108	3	3.9	[13]
Cyclohexane			5		
n-Hexane			5		
Benzene	760 Torr	54	3	2.9	[35]
Methylcyclopentane			3		
n-Hexane			3		
Cyclohexane	760 Torr	76	4	4.4	[36]
n-Heptane			2		
Toluene			3		
Ethanol	760 Torr	57	11	7.6	[37]
Methylcyclopentane			8		
n-Hexane			9		
Ethanol	50°C	19	13	6.1	[21]
Toluene			7		
Cyclohexane			7		
Ethanol	50°C	19	8	5.6	[11]
Benzene			11		
Cyclohexane			4		
Ethanol	300 Torr	19	10	3.3	[11]
Benzene			9		
Cyclohexane			6		
Ethanol	760 Torr	19	14	10.4	[11]
Benzene			5		
Cyclohexane			12		
Ethanol	760 Torr	47	22	15.7	[38]
Benzene			14		
n-Heptane			12		
Ethanol	400 Torr	50	14	6.1	[16]
Benzene			11		
n-Heptane			7		
Ethanol	180 Torr	55	8	1.1	[39]
Benzene			6		
n-Heptane			5		
Ethanol	760 Torr	41	10	6.6	[40]
Benzene			4		
n-Hexane			10		

Table 4 (Continued)

System	Temp. or press.	No. of data points	Arith. mean dev.		Ref.
			$ \Delta y $ ($\times 10^3$)	$ \Delta P $ (Torr)	
Ethanol	760 Torr	47	8	8.6	[26]
Benzene			4		
Methylcyclopentane			6		
Isopropanol	760 Torr	70	5	5.4	[27]
Benzene			4		
Cyclohexane			5		
Methanol	34.68°C	6	7	1.2	[30]
Benzene			5		
Carbon tetrachloride			4		
Methanol	55°C	8	13	6.1	[30]
Benzene			17		
Carbon tetrachloride			5		
n-Propanol	75°C	78	16	8.8	[41]
Benzene			15		
n-Heptane			12

Fig. 3. Comparison of calculated and experimental heat of mixing data for three binary systems at 25°C

Calculated —

Experimental

○ Ethanol(1)-cyclohexane(2) Ref. [43]

△ Cyclohexane(1)-benzene(2) Ref. [44]

● Ethanol(1)-benzene(2) Ref. [45]

Table 5. Calculated results for heat of mixing data of binary systems at 25°C

System	No. of data points	Arith. mean dev. β'		Ref.
		$ \Delta h^E $ (cal/mol)	(cal/cc)	
Ethanol-cyclohexane	15	4.3	3.341	[43]
Cyclohexane-benzene	29	2.1	7.808	[44]
Ethanol-benzene	10	20.7	0.715	[45]

data points. This relatively large deviation may be due to the fact that the theory did not represent correctly the experimental data for the ethanol-benzene mixture.

Application of the Proposed Equation to Other Alcohol-Active Solvent Mixtures. The present approach is applied to mixtures of alcohols and more active solvents than unsaturated hydrocarbons. Tables 6 and 7 give, respectively, the results of isothermal vapor-liquid equilibrium data and heat of mixing data for nine binary alcohol-active solvent systems. A survey of Table 6 indicates that calculated results are in substantial

Table 6. Calculated results for vapor-liquid equilibrium data of binary alcohol-active solvent mixtures

System	Basic data		T (°C)	No. of data points	Arith. mean dev.			Ref.
	K_{AB} ($T^\circ\text{C}$)	h_{AB} (kcal/mol)			$ \Delta y $ ($\times 10^3$)	$ \Delta P $ (Torr)	β (cal/cc)	
Methanol-ethyl acetate	290 (25)	-4.40	40	14	12.9	4.0	8.581	[46]
			50	13	8.6	2.6	7.399	[46]
			60	15	11.2	6.9	6.913	[46]
Ethanol-ethyl acetate	180 (25)	-4.40	40	18	18.6	2.9	10.750	[46]
			60	19	10.4	3.4	9.248	[46]
n-Propanol-ethyl acetate	100 (25)	-4.40	40	12	19.8	2.9	9.807	[46]
			60	14	7.9	2.9	7.857	[46]
Isopropanol-ethyl acetate	70 (25)	-4.40	40	14	10.1	2.0	8.618	[46]
			60	19	9.1	1.4	7.480	[46]
Methanol-methyl acetate	500 (25)	-4.40	35	14	10.6	3.6	14.206	[47]
			45	13	11.0	5.3	14.477	[47]
Ethanol-methyl acetate	300 (25)	-4.40	45	11	8.2	4.5	16.129	[47]
			55	13	12.0	10.9	15.644	[47]
Ethanol-ethyl ether	75 (20)	-4.20	0	19	4.0	2.3	3.863	[48]
			10	19	4.7	2.1	3.263	[48]
			20	19	6.9	3.4	2.972	[48]
			30	19	9.0	6.3	2.803	[48]
			40	19	11.9	12.8	2.638	[48]
			50	19	15.5	23.4	2.432	[48]
Methanol-acetone	350 (50)	-5.00	50	35	10.6	6.1	12.212	[49]
			55	14	7.1	6.9	12.677	[50]
Ethanol-acetone	200 (50)	-5.00	32	14	26.8	8.0	16.419	[51]
			40	14	24.8	8.5	15.741	[51]
			48	14	21.0	9.7	15.385	[51]

agreement with experimental data, although the ethanol—acetone system gives the poorest agreement and is probably an example of lowest accuracy and furthermore, the magnitudes of the deviations for the ethanol—ethyl ether system increase sharply with increasing temperature. Table 7 demonstrates that calculated heat of mixing data for the nine systems do not always agree well with experimental results. The same thing is found for the alcohol—unsaturated hydrocarbon systems [4].

Table 7. Calculated results for heat of mixing data of binary alcohol-active solvent mixtures

System	T (°C)	No. of data points	Arith. mean dev. $ \Delta h^E $ (cal/mol)	β' (cal/cc)	Ref.
Methanol-ethyl acetate	25	15	8.8	3.496	[52]
Ethanol-ethyl acetate	25	14	24.4	8.959	[52]
n-Propanol-ethyl acetate	25	19	23.6	10.873	[52]
Isopropanol-ethyl acetate	25	13	31.8	13.169	[52]
Methanol-methyl acetate	25	16	14.6	0.299	[53]
	35	16	16.8	1.455	[53]
	45	11	18.1	6.398	[47]
Ethanol-methyl acetate	25	12	29.0	7.078	[53]
	35	12	31.2	8.452	[53]
Ethanol-ethyl ether	25.15	8	11.6	0.563	[54]
Methanol-acetone	25.05	8	22.9	2.901	[54]
Ethanol-acetone	25.12	8	31.8	10.695	[54]

Conclusions

The original Kretschmer-Wiebe equation is extended to a ternary mixture including one alcohol and two hydrocarbons. Prediction of the excess Gibbs free energy data is successful for 18 ternary systems involved alcohol, hydrocarbon and carbon tetrachloride from only binary parameters. Ternary heat of mixing data for the ethanol—benzene—cyclohexane system is not predicted so accurately as the excess Gibbs free energy data. The proposed equation seems to be useful to correlate equilibrium data for binary mixtures of alcohols and active solvents such as esters and ketones.

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