

Thermodynamics of associated solutions

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学位論文要旨

ABSTRACT

An association model to treat the non-ideal behaviors of associated solutions, based on the new local composition model, is presented. The present model assumes the equilibrium constants for the formation of chemical complex defined in terms of the modified volume fractions of chemical species. The model is applied to describe the thermodynamic properties of binary and ternary vapor-liquid equilibria, liquid-liquid equilibria and excess enthalpies in alcohol mixtures, in acid mixtures, and in alcohol and acid mixtures using the association parameters obtained from their pure-component properties. In acetonitrile and amine mixtures, the ternary phase equilibria are predicted well using smaller values of the association constants than those estimated from their pure-component properties. The model can reproduce the equilibrium properties of binary and ternary mixtures containing acetonitrile and alcohol using the association constants estimated in this study. Furthermore, the model is applied to correlate binary vapor-liquid equilibria and to predict ternary phase equilibria in sulphur dioxide mixtures using only binary information. The predicted results for these ternary mixtures are in good agreement with the experimental data.

INTRODUCTION

Many researchers have proposed solution models to describe the thermodynamic properties of solutions containing self-associating components such as alcohols and acids. However, the solution model which is able to applied to various associated solutions such as alcohol, amine, acid and acetonitrile solutions using the physically reasonable association-constants is under development. Recently, Nagata et al. have developed a rather simple and more useful local composition model to reproduce well the temperature-dependence of mutual solubility data, ternary vapor-liquid and liquid-liquid equilibria, and quaternary liquid-liquid equilibria. In this research, a new associated-solution model to correlate and to predict the

phase equilibria and excess enthalpies of associated solutions is developed using the new local composition model, and the model is applied to describe the equilibrium properties of various associated solutions of alcohol, acid, acetonitrile, amine and sulphur dioxide.

THEORY

The key equations for describe the thermodynamic properties such as phase equilibria and excess molar enthalpies of mixtures are derived from the expression of the excess Gibbs free energy by use of the basic thermodynamic relations. The chemical model to calculate the excess Gibbs free energy of associated mixtures is expressed as the sum of the chemical and physical contribution term. The chemical contribution term involves equilibrium constants due to the association of like molecules and the solvation of unlike molecules studied here. The chemical contribution term in the new association model is derived on the basis of the new local composition model whose segment fractions of each component are modified, and the physical contribution term in the model is the Wilson-type equation. The association and solvation constants in the new chemical contribution term are defined using the modified segment fractions of chemical species, and their constants are expressed as

[1] For alcohol, amine, acetonitrile and sulphur dioxide molecules,

$$K_A = \frac{\phi'_{A_{l+1}}}{\phi'_{A_l} \phi'_{A_1}} : A_l + A_1 = A_{l+1} \quad (1)$$

[2] For acid molecules,

$$K_A = \frac{\phi'_{A_2}}{\phi'^2_{A_1}} : A_1 + A_1 = A_2 \quad (2)$$

[3] Between alcohol or amine molecules and acetonitrile or active-component molecule,

$$K_{AB} = \frac{\phi'_{A_l B_1}}{\phi'_{A_l} \phi'_{B_1}} : A_l + B_1 = A_l B_1 \quad (3)$$

[4] Between acetonitrile or sulphur dioxide and active-component molecule, and between alcohol and acid molecule,

$$K_{AB} = \frac{\phi'_{A_l B_1}}{\phi'_{A_l} \phi'_{A_1}} : A_l + B_1 = A_l B_1 \quad (4)$$

where the modified segment fraction of component I is defined by the molecular geometric-size parameter γ_i of pure component I.

$$\phi'_i = \frac{\gamma_i^{(2/3)} x_i}{\sum_{j=1}^n \gamma_j^{(2/3)} x_j} \quad (5)$$

Ternary phase equilibria and excess enthalpies are predicted using binary interaction parameters in the physical term, which are obtained by fitting the model to binary experimental data.

RESULTS AND CONCLUSIONS

In the chapter 1, the new associated-solution model which can be applied to associated solutions including one alcohol is developed. The association parameters of pure alcohols are estimated from their vapor pressures using the homomorph concept. Ethers are used as homomorphs of alcohols. The association constants of associated components, which were estimated in this study, are shown in Table 1. The new associated-solution model has a good workability in representing vapor-liquid equilibria and excess enthalpies for binary alcohol mixtures, and in predicting ternary phase equilibria and excess enthalpies for many alcohol mixtures from only binary parameters as shown in Figure 1 and Tables 2 and 3.

In the chapter 2, binary vapor-liquid equilibria and excess molar enthalpies in mixtures including amine and/or acetonitrile are correlated well using the model whose association constant of acetonitrile is physically reasonable for acetonitrile molecule. Predictions for the ternary phase equilibria and excess enthalpies of mixtures containing aniline and/or acetonitrile and for the ternary excess molar enthalpies of the n-butylamine + acetonitrile + 1, 4-dioxane system are in good agreement with the experimental results. A part of these results is shown in Tables 2 and 3 and Figure 2.

In the chapter 3, the model is further extended to treat many mixtures containing alcohol and acetonitrile. Vapor-liquid equilibria, liquid-liquid equilibria and excess enthalpies for binary and ternary mixtures of these two associated components are quite well represented using association constants estimated in this study, as shown in Tables 2 and 3 and Figure 2.

In the chapter 4, the model is applied to sulphur dioxide solutions with organic components and is found to predict ternary vapor-liquid equilibria and liquid-liquid equilibria with good accuracy. Ternary predicted liquid-liquid equilibria calculated using the model are better than those obtained from another model whose equilibrium constants are defined in terms of the mole fractions of chemical species.

In the chapter 5, the dimerization parameters of acid molecules were estimated from the vapor-pressures of pure acids using the homomorph concept. Methyl alkanoates are adopted as homomorphs of acids. The binary vapor-liquid equilibria and excess enthalpies of alkanolic acid mixtures are correlated well with the model. The model has a good workability in predicting ternary vapor-liquid equilibria of the acetic acid + toluene + n-heptane system, ternary liquid-liquid equilibria of alkanolic acid mixtures including water and a non-associated component using only binary parameters.

Table 1 Association constants K_A and enthalpies ΔH_A for complex formation

Component	K_A (at 50°C)	$-\Delta H_A$ /kJ mol ⁻¹	Component	K_A (at 50°C)	$-\Delta H_A$ /kJ mol ⁻¹
Methanol	143.0	22.5	Acetonitrile	0.8	6.7
Ethanol	119.2	22.2	Aniline	10.0	9.0
1-Propanol	104.3	22.0	n-Butylamine	2.0	9.0
2-Propanol	84.6	22.2	Sulphur dioxide	1.5*	6.6
1-Butanol	95.6	21.5	Formic acid	25457.	42.4
2-Butanol	68.6	20.8	Acetic acid	23357.	43.9
iso-Butanol	78.7	21.2	Propionic acid	19680.	45.4
tert-Butanol	38.1	19.7	Butyric acid	18840.	46.9

*) K_A of sulphur dioxide is 1.5 at 0°C.

Furthermore, in the chapter 6, the binary vapor-liquid equilibria and excess enthalpy data for alcohol + acid mixtures are well correlated using the present model and UNIQUAC associated-solution model whose solvation constants are defined by 1 : 1 complex formation between alcohol and acid molecules. The ternary excess molar enthalpies of methanol+ acetic

Table 2 Ternary predicted results for vapor-liquid equilibria

System (A+B+C)	Temp. /°C	No. of data points	Abs. arith. mean dev.*			
			δy_A $\times 10^3$	δy_B $\times 10^3$	δy_C $\times 10^3$	δP /Torr
Methanol + CCl ₄ + benzene	55	8	1.9	3.0	2.8	2.4
Ethanol + benzene + cyclohexane	55	19	7.1	4.8	8.4	5.6
1-Propanol + acetonitrile + benzene	55	27	5.4	7.4	6.3	3.4
2-Propanol + acetonitrile + benzene	50	23	4.4	3.2	4.5	4.3
2-Propanol + benzene + cyclohexane	40	6	6.3	2.1	5.5	1.5
1-Butanol + acetonitrile + benzene	60	15	2.6	7.2	7.5	4.5
2-Butanol + acetonitrile + benzene	60	21	3.4	4.3	5.2	3.6
iso-Butanol + acetonitrile + benzene	60	21	5.0	4.8	8.4	5.3
tert-Butanol + acetonitrile + benzene	60	27	3.9	3.9	5.5	2.4
Aniline + benzene + cyclohexane	70	10	0.5	7.8	7.4	3.1
Aniline + toluene + methylcyclohexane	80	7	1.1	3.1	3.0	3.7
Acetonitrile + benzene + n-heptane	45	51	8.4	3.3	6.6	3.9
Acetonitrile + benzene + CCl ₄	45	62	7.8	4.4	5.7	2.2
SO ₂ + benzene + n-pentane	-17.8	82	9.5	0.7	9.3	7.3
Acetic acid + toluene + n-heptane	30	47	8.8	7.5	11.3	1.9

* y, vapor-phase mole fraction; P, total pressure.

Table 3 Ternary predicted results for excess molar enthalpies H^E

System (A+B+C)	Temp. /°C	No. of data points	Abs. arith. mean dev.	
			δH^E /J mol ⁻¹	$\delta H^E/H^E$ /%
Methanol + 2-propane + benzene	25	57	13.60	2.70
Methanol + acetonitrile + benzene	25	57	27.36	3.60
Ethanol + p-xylene + cyclohexane	25	59	9.58	1.50
Ethanol + 2-propane + benzene	25	57	10.60	1.57
Ethanol + 2-butanone + benzene	25	42	14.40	2.46
1-Propanol + 2-propanone + benzene	25	57	8.31	1.12
1-Propanol + acetonitrile + benzene	25	56	13.68	1.30
2-Propanol + toluene + cyclohexane	25	56	10.55	1.47
2-Propanol + acetonitrile + benzene	25	57	17.56	1.57
1-Butanol + benzene + cyclohexane	25	43	15.46	1.58
2-Butanol + acetonitrile + benzene	25	65	26.34	1.60
iso-Butanol + acetonitrile + benzene	25	70	15.97	1.10
tert-Butanol + acetonitrile + benzene	30	60	27.19	1.77
Acetonitrile + benzene + CCl ₄	25	54	12.32	
Aniline + acetonitrile + benzene	25	52	18.91	
n-Butylamine + acetonitrile + 1,4-dioxane	25	53	23.65	
Acetic acid + methanol + CCl ₄	25	47	23.90	

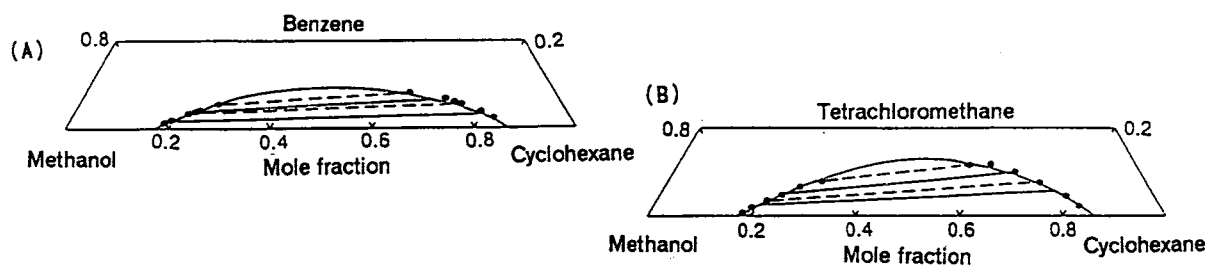


Fig. 1. Ternary liquid-liquid equilibria for alcohol mixtures.

Calculated.—. Experimental tie-line : ●— —●, (A) methanol + benzene + cyclohexane at 25°C; (B) methanol + CCl₄ + cyclohexane at 25°C.

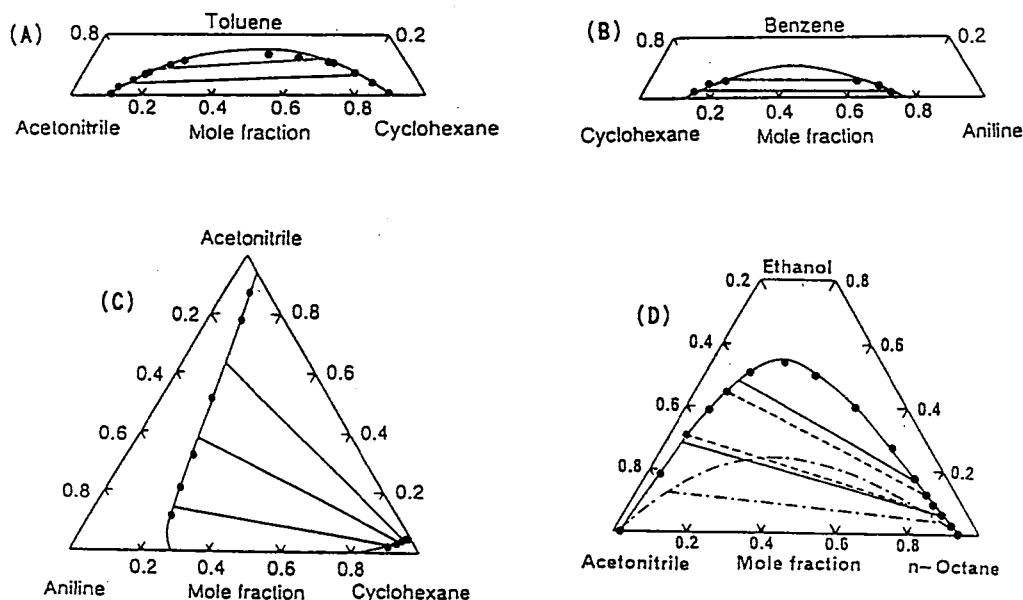


Fig. 2 Ternary liquid-liquid equilibria for acetonitrile and/or aniline mixtures. Calculated.—. Experimental tie-line data : ●, (A) acetonitrile + toluene + cyclohexane at 45°C; (B) cyclohexane + benzene + aniline at 20°C; (C) aniline + acetonitrile + cyclohexane 25°C; (D) ethanol + acetonitrile + n-octane at 25°C : - - - - - , calculated results without association of acetonitrile molecules.

acid + tetrachloromethane are reasonably well predicted from the binary data.

In conclusion, the proposed associated-solution model is able to be applied to many kinds of associated solutions such as alcohol, amine, acetonitrile, sulphur dioxide and alkanolic acid solutions with good accuracy.

学位論文の審査結果の要旨

平成 8 年 1 月 30 日、本論文の発表会終了後審査委員会を開催し、発表及び論文内容について討議し次の如く判定した。

新しい局所モル組成式に基づいた会合モデルを展開して、アルコール、酸、アセトニトリル、アミン、及び二酸化硫黄のこれらの混合溶液の気液平衡、液液平衡、混合熱データの解析を行った。会合定数を修正セグメント分率で定義し、会合による分子の数に因らないと仮定した。アルコールと酸の

会合定数の値と水素結合のエンタルピーの値を蒸気圧データと異質同像の概念を使って求めた。又、他の弱会合性成分の会合定数の値を混合溶液の物性値を良く表現できるように決定した。

第一章ではアルコール溶液の二成分系気液平衡と混合熱を正確に表現できることを示し、更に二成分パラメータのみを使って三成分系の気液平衡、液液平衡及び混合熱の推算を行い、多くの例でその有効性を実証した。尚、アルコールとケトン、エステル等の活性成分との間に溶媒和定数を導入した。

第二章ではアミンとアセトニトリルのそれぞれの溶液についても同様な解析を行い、二成分系データの相関のみならず三成分系データの推算にもモデルが有効であることを示した。

第三章ではアルコールとアセトニトリルの混合溶液に対し、両成分とも会合するモデルに拡張した。特に三成分系液液平衡の推算ではアセトニトリルの会合を考慮した時の方が良い結果を得ることを示した。

第四章では二酸化硫黄溶液の相平衡データの相関と推算を行い、特に三成分系液液平衡の推算では会合定数をモル分率で定義したモデルより本研究のセグメント分率モデルの方が良い結果を得た。

第五章では酸と有機化合物との相平衡と混合熱の解析を行い、且、酸の水溶液の液液平衡の推算でも良い結果を得た。

第六章ではアルコール+酸溶液の二成分系気液平衡と混合熱の解析に成功した。

以上の結果より本論文の内容は博士(工学)を授与するに値すると判定する。