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Application of Transient State Theory of Significant Liquid Structure to Binary Mixtures

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이성분 용액에 대한 "천이상태이론"의 적용

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요 약

이성분 용액에 대한 천이상태 이론의 적용 방법을 재고찰하여 이론적 보충을 하여주었으며, 이 새로운 방법에 따라서 C_6H_{12}—CCl_4계의 열역학적 성질들을 계산하였다. 또한 전의 방법에 따라서 계산된 C_6H_6—C_6H_{12} 및 C_6H_6—CCl_4계의 열역학적 성질들도 재계산하였다.

이 방법에 따라서 계산된 열역학적 성질들은 측정치와 대단히 잘 맞는다.

I. Introduction

H. Eyring et al applied the "Signficant Liquid Structure Theory" [1][2] to the binary liquid system of various kinds by introducing several characteristic parameters for the binary mixing. [3][4]

S. Chang et al applied both the "Significant Liquid Structure Theory" and the "Transient State Theory"[5] to the binary mixtures without introducing extra parameter, but just by combining the partition functions for each component. [6][7][8] However, this method implies the result that the composition of liquid is same as that of gas in equilibrium, which is apparently wrong, since the more volatile component is richer in the gaseous phase than in the liquid phase.

The authors have revised the method as described below, and applied to C_6H_{12}—CCl_4 system according to the "Transient State Theory" and redetermined the thermodynamic properties for the systems, C_6H_6—C_6H_{12}[7] and C_6H_6—CCl_4[8], which were previously calculated according to the old method.

II. Formulation of partition function

A. Partition functions for the component liquids

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According to the "Transient State Theory", liquid molecules acquire gas-like property by jumping into neighboring fluidized holes only through the transient state. And when a molecule vibrates at an equilibrium position, it has solid-like property. Therefore, liquid molecules have three kinds of degree of freedom; namely, the gas-like, the transient, and solid-like.

Since, in a liquid, $N(V-V_s)/V_s$ holes are introduced among N molecules, the fraction of gas-like molecules is

$$(V_s/V)(V-V_s)/V_s=(V-V_s)/V=1-1/x,$$

where V and V_s are the molar volumes of liquid and of solid at the melting point, respectively, and $x=V/V_s$; then, $N(V_s/V)$ molecules must be bonded to each other.

Therefore, among N molecules, $N(V-V_s)/V$ molecules have gas-like degree of freedom, and the remaining $N(V_s/V)$ molecules are partitioned among the solid-like and the transient degrees of freedom in such a manner that $\alpha N(V_s/V)$ and $(1-\alpha)N(V_s/V)$ are the numbers of molecules possessing solid-like and transient degrees of freedom, respectively; here, α is a fractional number.

Then, the partition functions for benzene, cyclohexane, and carbon tetrachoride, according to the "Transient Sta te Theory", are written [5][6][8] as

$$F=\frac{(N\frac{1}{x})!}{(N\frac{1}{x}\alpha)!\,[N\frac{1}{x}(1-\alpha)]!}\left\{\frac{e^{Es/RT}}{(1-e^{\theta s/T})^3}b_s\right\}^{N\frac{1}{x}\alpha}\left\{\frac{(E_s-\frac{aEs}{n(x-1)})\frac{1}{RT}}{\frac{n(x-1)e}{(1-e^{-\theta t/T})^3}}b_t\right\}^{N\frac{1}{x}(1-\alpha)}\left\{\frac{(2\pi mkT)^{3/2}}{h^3}\frac{eV}{N}b_g\right\}^{N(1-\frac{1}{x})} \quad (1)$$

where,

$$b_s=b_t=b_g=\frac{\sqrt{\pi}(8\pi^2kT)^{3/2}(I_AI_BI_C)^{1/2}}{\sigma h^3}\cdot\prod_i\frac{1}{(1-e^{-h\nu i/kT})} \quad (1-a)$$

However, for benzene b_s and b_t are expressed as shown below, because the free rotation of benzene molecules in solid and transient states are restricted.

$$b_s=\frac{1}{(1-e^{-\theta S/T})^3}\prod_i\frac{1}{(1-e^{-h\nu i/kT})} \quad (1-b)$$

$$b_t=\frac{1}{(1-e^{-\theta t/T})^3}\prod_i\frac{1}{(1-e^{-h\nu i/kT})} \quad (1-c)$$

Here, E_s and θ are the parameters which correspond to the heat of sublimation at the ground state and the Einstein's characteristic temperature, respectively. Subscripts, s, t, and g, denote the solid-like, transient, and gas-like states, respectively. aEs/n $(x-1)$ is the strain energy, where, a is a proportionality constant, and n is the number of the nearest neighboring sites around a molecule. σ is a symmetry number. The other symbols in the partition function have their ususl physical meanings.

The parameters determined and the values for characteristic symboles in the expression are shown in Table 1.

Table 1. Values for parameters and characteristic symbols. [6][7][8]

	C_6H_6	C_6H_{12}	CCl_4
E_s(Cal/Mole)	1,035.0	8,823.16	8,743.3
θ_s(°K)	56.515	76.271	57.300
θ_t(°K)	49.041	75.146	54.539
a ($\times10^2$)	4.524	3.187	2.047
n	10.585	11.301	11.483
V_s(cm^3)	77.00	100.19	87.9
σ	12	6	12

B. The partition function for a binary solution

In formulating the partition function for a binary solution, it is assumed that the solid-like and the transient molecules of both components are distributed in a random fashion, and that the gas-like molecules of both components are indistinguishable.

Accordingly, the partition function for a binary solution can be written as

$$F_{soln}=\frac{(N_{s1}+N_{s2}+N_{t1}+N_{t2})!}{N_{s1}!\,N_{s2}!\,N_{t1}!\,N_{t2}!}f_{s1}^{Ns1}f_{s2}^{Ns2}f_{t1}^{Nt1}f_{t2}^{Nt2}f_{g1}^{Ng1}f_{g2}^{Ng2}\frac{1}{N_{g1}!\,N_{g2}!} \quad (2)$$

The total number of holes available to the i-th component molecules in a mole of solution can be given by

$$N\frac{V-V_s}{V_{si}^\circ}=(x_i-1)N \quad (3)$$

Here, $x_i=(V-V_s+V_{si}^\circ)/V_{si}^\circ$; V_s being the molar volume of the solid-like molecules which can be given as

$$V_s=\xi_iV_{si}^\circ+\xi_jV_{sj}^\circ$$

where, ξ_i is the mole fraction of the i-th component; V_{si}° being solid molar volume at the melting point of the i-th component in its pure state.

From equation (3), the following expression is obtainable.

$$(x_i-1)V_{si}^{\circ}=(x_j-1)V_{sj}^{\circ} \quad (4)$$

Accordingly, the number of the gas-like molecules of the i-th component can be given by

$$N\xi_i\frac{(x_i-1)N}{N(x_i-1)+N}=N\xi_i(1-\frac{1}{x_i}) \quad (5)$$

Then, the number of molecules for each degree of freedom can be obtained explicitly.

From the fact that the free energy of a system becomes minimum at an equilibrium, the following relationship can be obtained.

$$\alpha_i=\frac{f_{si}}{f_{si}+f_{ti}} \quad (6)$$

Substituting equation (6) into equation (2) and using the Stirling's approximation, the following expression is obtained.

$$F_{soln}=\frac{(N\xi_1\frac{1}{x_1}!+N\xi_2\frac{1}{x_2})!}{(N\xi_2\frac{1}{x_1})!(N\xi_1\frac{1}{x_2})!}\cdot$$

$$F_{s1}^{N\xi_1\frac{1}{x_1}}F_{s2}^{N\xi_2\frac{1}{x_2}}F_{g1}^{N\xi_1(1-\frac{1}{x_1})}F_{g2}^{N\xi_2(1\xi\frac{1}{x_2})} \quad (7)$$

where,

$$F_{si}=\frac{e^{Esi/RT}}{(1-e^{-\theta si/T})^3}\{1+\lambda_i(x_i-1)\cdot \exp^{-\frac{a_iE_{si}}{n_i(x_i-1)RT}}\}b_{si}$$

$$F_{gi}=\frac{(2\pi m_ikT)^{3/2}\ e(V-V_s+V_{si}^{\circ})}{h^3N\xi_i}b_{gi}$$

$$\lambda_i=n_i\left\{\frac{1-e^{-\theta si/T}}{1-e^{-\theta ii/T}}\right\}^3\frac{b_{ti}}{b_{si}}$$

Here, b_{si}, b_{ti}, and b_{gi} take the same expressions as equations (1−a), (1−b), and (1−c), depending on the kind of the i-th component molecules.

III. Calculation of thermodynamic properties

The values for parameters, θ_{si}, θ_{ti}, a_i and n_i are assumed to be independent of the composition in the solution; therefore, the values shown in Table 1 are used for this work.

However, E_{si}, the parameter corresponding to the heat of solid-like molecules of the i-th components in the solution, can be expressed as

$$E_{si}=\frac{1}{2}\phi_{ii}n_i\xi_i+\frac{1}{2}\phi_{ij}n_i'\xi_j=E_{si}^{\circ}\xi_i+E_{sij}\xi_j \quad (8)$$

where,

$$E_{sij}=\frac{1}{2}\phi_{ij}n_i'$$

where, ϕ_{ii} and ϕ_{ij} are the molar binding energies between the pair of similar molecules and that of dissimilar molecules, respectively. n_i and n_i' are the coordination number for a molecule of the i-th component, assuming that the surrounding molecules are of the i-th component alone and that the surrounding molecules are of the j-th component alone, respectively.

E_{sij} for C_8H_{12}—CCl_4 solution is calculated by the method developed by W. Ahn[7], using the literature values for the energy of mixing[9]; and E_{sij} values for C_6H_6—C_6H_{12} and C_6H_6—CCl_4 solutions are taken from the previous works by W. Ahn[7] and by S. Chang et al[8], respectively.

The values for E_{sij} at three different temperatures are shown in Table 2.

Table 2. The values for E_{sij} (cal/mole)

Temp. (°K)	298.15	303.15	313.15	343.15
C_6H_6—C_6H_{12}		9,339.6	9,337.0	9,329.2
C_8H_{12}—CCl_4	8,732.6		8,735.4	8,742.0
C_6H_6—CCl_4	9,487.9		9,492.5	9,499.1

A. The molar volume and the vapor pressures

The vapor pressure of a pure liquid in equilibrium with its own vapoer pressure can be obtained from the negative slope of the common tangential line between liquid region and the gaseous region, $-(\Delta A/\Delta V)$, using the followng thermodynamic relationships.

$$A=-kT\ln F \quad (9)$$

$$P=-(\partial A/\partial V)_T \quad (10)$$

The same method for the theoretical determination of the total vapor pressure for the binary mixture has been so far employed[6][7][8].

However, in the case of binary liquid solution, the compositions for the vapor and liquid are different; therefore, the plot of Helmholtz free energy against molar volume at the constant liquid mole fraction is not significant in the vapor region.

For this work the defect is eliminated and the following new method is used.

1. The value for slope, $-(\partial A/\partial V)_{T,\xi}$, is plotted against molar volume at the very vicinity of the expected total vapor pressure of the solution, as indicated by P_T in Fig. 1.

2. Using the equation,

$P_i = p_i^0 \exp\{(\mu_i - \mu_i^0)/kT\}$

partial pressures for both components are calculated. Then, as shown in Fig. 1, P_1+P_2 against molar volume is plotted.

3. The joining point of the two curves, P_T and P_1+P_2 will give the total vapor pressure, the molar volume and the partial pressures of the solution.

The calculated values for the molar volumes, the partial pressures for each component, and the total pressures, are shown in columns 2, 3, 4, and 5, respectively, in Tables 3, 4, and 5.

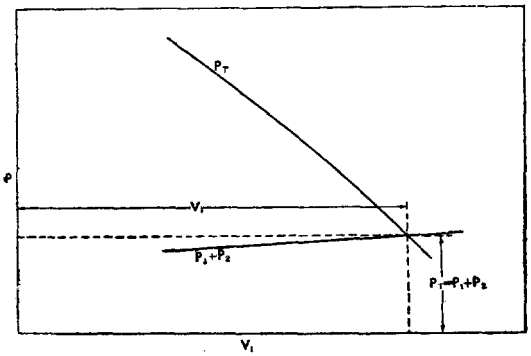

Figure 1. Schematic representation of vapor pressure vs. molar volume curve

Table 3. Various thermodynamic properties of C_6H_{12}—CCl_4 system

ξ_1	M. V. (cc)	P_1(atm)	P_2(atm)	P_T(atm)	ΔS_{mix}(eu)
(at 298.15°K)					
0.0	96.69	0.0000	0.1490	0.1490	0.0000
0.2	99.28	0.0283	0.1199	0.1482	1.0023
0.4	101.88	0.0547	0.0905	0.1452	1.3497
0.5	103.17	0.0672	0.0773	0.1445	1.3903
0.6	104.47	0.0795	0.0629	0.1424	1.3504
0.8	107.04	0.1046	0.0328	0.1374	1.0033
1.0	109.59	0.1288	0.0000	0.1288	0.0000
(at 313.15°K)					
0.0	98.19	0.0000	0.2812	0.2812	0.0000
0.2	100.89	0.0530	0.2261	0.2791	0.9869
0.4	103.56	0.1019	0.1724	0.2743	1.3387
0.5	104.90	0.1254	0.1454	0.2708	1.4404
0.6	106.24	0.1486	0.1181	0.2667	1.3452
0.8	108.91	0.1947	0.0613	0.2560	0.8280
1.0	111.51	0.2417	0.0000	0.2417	0.0000
(at 343.15°K)					
0.0	101.56	0.0000	0.8219	0.8219	0.0000
0.2	104.40	0.1546	0.6605	0.8151	0.9907
0.4	107.23	0.3078	0.4933	0.8011	1.3428
0.5	108.60	0.3704	0.4222	0.7926	1.3781
0.6	110.06	0.4402	0.3417	0.7819	1.3487
0.8	112.88	0.5799	0.1760	0.7552	1.0075
1.0	115.72	0.7207	0.0000	0.7207	0.0000

Table 4. Various thermodynamic properties of C_6H_6—C_6H_{12} system

ξ_1	M. V. (cc)	P_1(atm)	P_2(atm)	P_T(atm)	ΔS_{mix}(eu)
(at 303.15°K)					
0.0	110.21	0.0000	0.1591	0.1591	0.0000
0.2	106.84	0.0466	0.1331	0.1797	1.1500
0.4	102.88	0.0778	0.1097	0.1875	1.5395
0.5	100.77	0.0910	0.0973	0.1883	1.5761
0.6	98.59	0.1029	0.0843	0.1872	1.5216
0.8	94.07	0.1276	0.0512	0.1788	1.1139
1.0	89.32	0.1561	0.0000	0.1561	0.0000
(at 313.15°K)					
0.0	111.51	0.0000	0.2417	0.2417	0.0000
0.2	108.02	0.0704	0.2017	0.2721	1.1339
0.4	103.97	0.1184	0.1652	0.2836	1.5196
0.5	101.82	0.1383	0.1469	0.2852	1.5567
0.6	99.61	0.1573	0.1263	0.2836	1.5030
0.8	95.02	0.1955	0.0761	0.2716	1.0986
1.0	90.24	0.2392	0.0000	0.2392	0.0000
(at 343.15°K)					
0.0	115.72	0.0000	0.7207	0.7207	0.0000
0.2	111.84	0.2049	0.5981	0.8030	1.0983
0.4	107.56	0.3511	0.4861	0.8372	1.4790
0.5	105.29	0.4133	0.4286	0.8419	1.5452
0.6	102.96	0.4723	0.3668	0.8391	1.4736
0.8	98.13	0.5901	0.2177	0.8078	1.0772
1.0	93.17	0.7240	0.0000	0.7240	0.0000

Table 5. Various thermodynamic properties of C_6H_6—CCl_4 system

ξ_1	M. V. (cc)	P_1(atm)	P_2(atm)	P_T(atm)	ΔS_{mix}(eu)
(at 298.15°K)					
0.0	96.69	0.0000	0.1490	0.1490	0.0000
0.2	95.48	0.0268	0.1216	0.1484	1.0523
0.4	94.06	0.0516	0.0940	0.1456	1.4124
0.5	93.28	0.0636	0.0798	0.1434	1.4486
0.6	92.47	0.0755	0.0652	0.1407	1.3996
0.8	90.77	0.1004	0.0347	0.1351	1.0203
1.0	88.97	0.1246	0.0000	0.1246	0.0000
(at 313.15°K)					
0.0	98.19	0.0000	0.2812	0.2812	0.0000
0.2	96.94	0.0506	0.2288	0.2794	1.0523
0.4	95.47	0.0981	0.1762	0.2743	1.4161
0.5	94.68	0.1213	0.1493	0.2706	1.4560
0.6	93.85	0.1444	0.1216	0.2660	1.4077
0.8	92.11	0.1910	0.0635	0.2545	1.0393
1.0	90.27	0.2391	0.0000	0.2391	0.0000
(at 343.15 °K)					
0.0	101.56	0.0000	0.8218	0.8218	0.0000
0.2	100.17	0.1494	0.6742	0.8236	1.0193
0.4	98.60	0.2933	0.5105	0.8038	1.3716
0.5	97.75	0.3642	0.4307	0.7949	1.4116
0.6	96.88	0.4350	0.3494	0.7844	1.3691
0.8	95.06	0.5777	0.1803	0.7580	1.0142
1.0	93.14	0.7239	0.0000	0.7239	0.0000

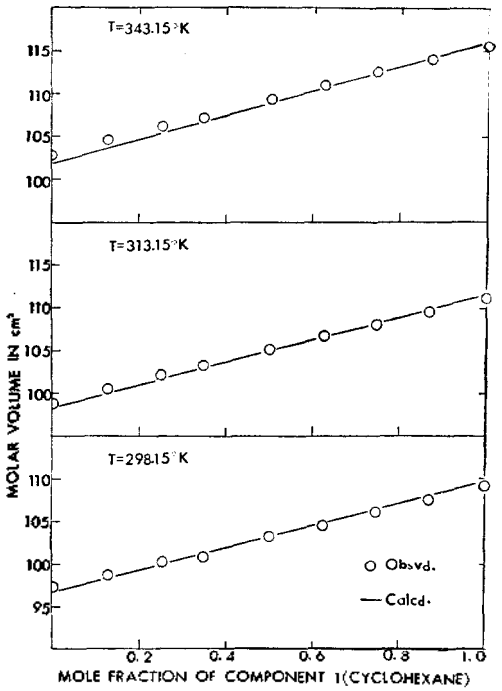

Figure 2. Molar volumes of C_6H_{12}—CCl_4 system

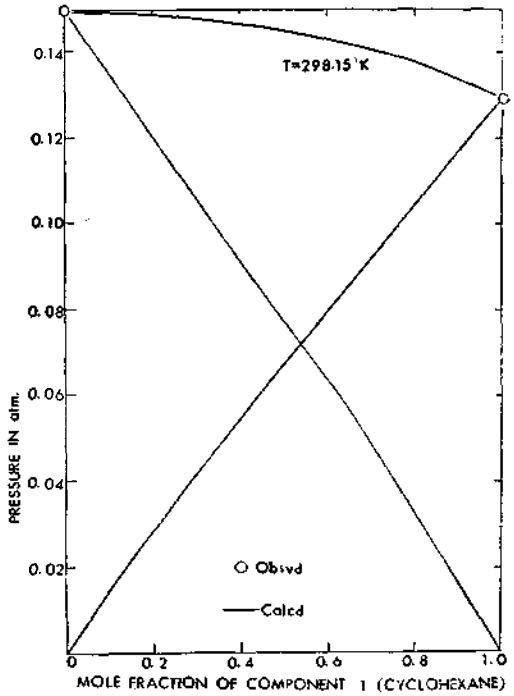

Figure 3. Vapor pressures of C_6H_{12}—CCl_4 system at 298.15°K

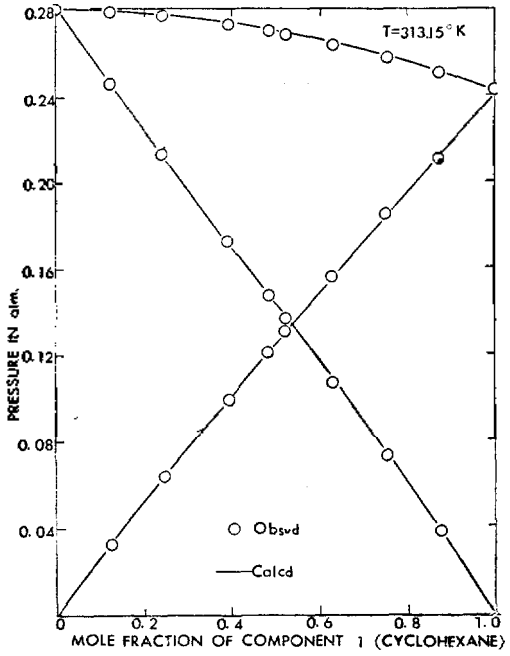

Figure 4. Vapor pressures of C_6H_{12} —CCl_4 system at 313.15°K

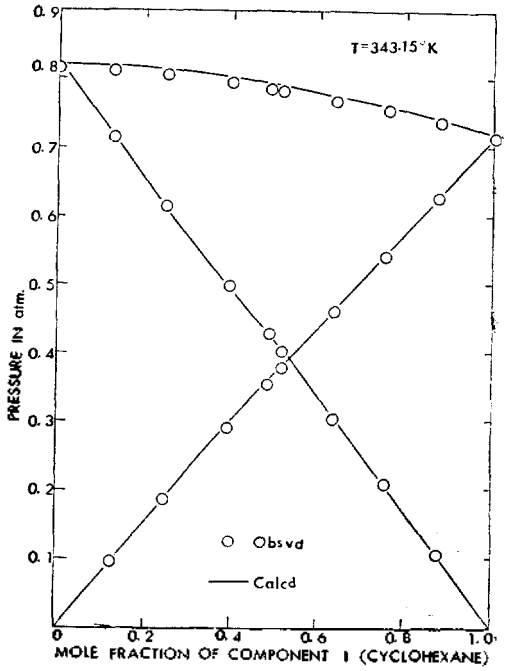

Figure 5. Vapor pressures of C_6H_{12}—CCl_4 system at 343°15K

B. The entropy of mixing

The entropy of mixing is calculated using the following thermodynamic relations.

$$S=-(\partial A/\partial T)_{V,t}$$

and

$$\Delta S_{mix}=S_{soln}-(\xi_1 S_1^0+\xi_2 S_2^0)$$

The calculated values for the entropy of mixing are shown in column 6 of Table 3, 4, and 5.

IV. Discussion

For this work the parameters, except E_{si}, in the combined partition function for solution; i.e., θ_{si}, θ_{ti}, a_i, and n_i are assumed to be independent of the composition of the solution. The values for the parameters may slightly change with respect to the composition of the solution, since the environment of a molecule is different when the composition of the solution is altered.

However, in view of the fact that the theoretical work under this assumption agree well with the experimental observation, the change of parametric values due to the environmental change should be negligibly small. Moreover, it is expected that the change of parametric values with environmental change must be further minimized, if the solution is nearly isomegatic and the interaction between dissimilar molecules are nearly same as that between similar molecules, as it is the case for this work.

Although the difference between the value of the total pressure and that of the sum of partial pressures for the C_6H_6—C_6H_{12} and C_6H_6—CCl_4 solutions is not more than one percent in the works by W. Ahn[7] and by S. Chang et al[8], which is within the acceptable calculation error, it is not theoretically acceptable to presume that the composition of liquid and that of the vapor in its equilibrium are the molar volume.

In this work, this theoretical defect is eliminated; and a revised method as decribed before is used.

As shown in Fig. 2, 3, 4, and 5, the theoretical calculations agree well with the experimentally observed values[10]. However, there shows slight deviation in the work at higher temperatures. This is attributed to defect of the partition functions of pure component liquids.

The calculated mixing entropy shows ideality which is reasonable, in view of the fact that the molecules of C_6H_{12} and CCl_4 are very neary spherical and that the excess molar volume shows zero in both experimental and theoretical results.

The recalculated data for the C_6H_6—C_6H_{12} and C_6H_6—CCl_4 solutions, which are very close to those obtained in the previous works by W Ahn[7] and S. Chang et al[8], agree well with the observed values.

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