

Significant Liquid Structure of Binary Mixture, $C_6H_6-C_2H_4Cl_2$.

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이성분 액체 혼합물의 통계열역학적 연구

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요 약

벤젠—염화에틸렌 이성분 용액에다 significant liquid structure theory를 확장 적용시켰다. 라울의 법칙이 만족되는 온도 범위 안에서 적용되는 분배함수를 구하였다. 이 분배함수로 부터 계의 전체압, 부분압, 몰부피 그리고 혼합엔트로피와 같은 열역학적 양을 293.15°, 323.14° 및 357.15°K에서 계산하였다. 이와 같이 구한 이론적인 계산치들은 실측치와 대단히 잘 맞았다.

Abstract

The significant liquid structure theory is extended to binary mixture, benzene—ethylenechloride system. The partition function, applicable throughout the temperature range in which Raoult's law is satisfied is derived. The thermodynamic quantities such as total and partial pressures, molar volumes and mixing entropies are calculated from the partition function at the temperatures 293.15°, 323.14° and 357.15°K. The theoretical values, thus calculated, are found to agree with the experimental data in the literatures.

Introduction

The partition functions for various substances in liquid state can easily be derived by the significant liquid structure theory, developed by Henry Eyring and his coworkers.¹⁻⁴⁾ It is also well known that the thermodynamic quantities calculated from the partition function are in good agreement with the experimentally observed values.

The theory has been extended to binary mix-

tures by introducing a number of parameters by K. Liang, H. Eyring, R. Marchi and S. Ma.^{5,6)} The authors, however, extended the theory to binary mixtures in different manner without introducing extra parameters, and applied it to benzene—ethylenechloride liquid solution. Literature shows the liquid mixture obeys the Raoult's law from about 290° to 350°K.^{7,8)}

According to the significant liquid structure theory, a liquid molecule possesses both the solid-like and gas-like degrees of freedom. A molecule around the vacant hole in the liquid assumes the

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gas-like degree of freedom when it jumps into the hole. With the above consideration, the partition functions for benzene and for ethylenechloride were derived previously, using the modified significant structure theory, as follows.^{4,9)}

$$f_{C_6H_6} = \left[\frac{e^{E_s/RT}}{(1 - e^{-\theta/RT})^6} \left\{ 1 + n(x-1)e^{-\frac{aE_s}{n(n-1)RT}} \right\} \frac{1}{\prod_{D6h}} \right]^{N \frac{1}{x}} \left[\frac{(2\pi mkT)^{3/2} eV}{h^3 N} \cdot \frac{\sqrt{\pi}(8\pi^2 kT)^{3/2} (I_A I_B I_C)^{1/2}}{12h^3} \frac{1}{\prod_{D6h}} \right]^{N(1-\frac{1}{x})} \dots \dots \dots (1)$$

$$f_{C_2H_4Cl_2} = \left[\frac{e^{E_s/RT}}{(1 - e^{-\theta/RT})^6} \left\{ 1 + n(x-1)e^{-\frac{aE_s}{n(n-1)RT}} \right\} \frac{1}{\prod_{C2h}} \right]^{N \frac{1}{x}} \left[\frac{(2\pi mkT)^{3/2} eV}{h^3 N} \cdot \frac{\sqrt{\pi}(8\pi^2 kT)^{3/2} (I_A I_B I_C)^{1/2}}{2h^3} \frac{1}{\prod_{C2h}} \right]^{N \frac{NC_2h}{NC_2 + NC_2h}} \left[\frac{\sqrt{\pi}(8\pi^2 kT)^{3/2} (I_A' I_B' I_C')^{1/2}}{h^3} \frac{1}{\prod_{C_2}} \right]^{N(1-\frac{1}{x})} \dots \dots \dots (2)$$

$$\prod_{D6h} = \prod_{i=1}^{30} (1 - e^{-h\nu_i/RT})$$

$$\prod_{C2h} = \prod_{i=1}^{18} (1 - e^{-h\nu_i/RT}) \dots \dots \dots (3)$$

$$\prod_{C_2} = \prod_{i=1}^{18} (1 - e^{-h\omega_i/RT})$$

where E_s and θ are parameters corresponding to the heat of sublimation and Einstein characteristic temperature of the solid-like molecules, respectively. "a", in the strain energy term $aE_s V_s / n(V - V_s)$, is also a parameter. V_s is the molar volume of the molecule having the solid-like degree of freedom, and its ratio to the liquid molar volume is denoted by $1/x$, which turns out to be the fraction of the solid-like molecules.⁴⁾ "n" is the number of the nearest neighboring sites around a molecule. The values of the parameters are given in Table I. R , k , N , T and h are usual physical constants. I_A , I_B , I_C are the three principal moment of inertia. μ_i , ν_i and ω_i are the i -th internal frequency of benzene, *trans*-form of ethylenechloride and *gauche*-form

of ethylenechloride molecules, respectively.

Table I The Parameters.

	$\theta^\circ K$	$E_s, \text{cal/mol}$	a	V_s, cc	n
C_6H_6	44.354	9636.1	0.014389	82.826	11.386
$C_2H_4Cl_2$	23.381	9405.9	0.0010958	73.222	11.842

Partition Function

In formulating the complete partition function for the mixture, we have assumed that the solid-like molecules are mixed in a random manner, and that the parameters θ , a , and n do not change upon mixing. The molar volumes of the solid-like molecules of the components are also assumed to be independent of the composition. That is the partial molar volumes of the solid-like molecules of a component is taken to be same as the molar volume at pure state. Then, the mean molar volume of the solid-like molecules of the mixture is given as follows:

$$V_s = \xi_1 V_{s1}^0 + \xi_2 V_{s2}^0 \dots \dots \dots (4)$$

where ξ is the mole fraction of a component, and the superscript zero denotes the pure component. The subscript 1 and 2 represent benzene (component one) and ethylenechloride (component two) respectively.

The complete partition function for the mixture consists of combinatorial factors, two solid-like parts and two gas-like parts;

$$F = \frac{(N\xi_1 \frac{1}{x_1} + N\xi_2 \frac{1}{x_2})!}{(N\xi_1 \frac{1}{x_1})! (N\xi_2 \frac{1}{x_2})!} f_{1s}^{N\xi_1 \frac{1}{x_1}} f_{2s}^{N\xi_2 \frac{1}{x_2}} f_{1g}^{N\xi_1(1-\frac{1}{x_1})} \frac{1}{[N\xi_1(1-\frac{1}{x_1})]!} f_{2g}^{N\xi_2(1-\frac{1}{x_2})} \frac{1}{[N\xi_2(1-\frac{1}{x_2})]!} \dots \dots \dots (5)$$

The combinatorial factor,

$(N\xi_1 \frac{1}{x_1} + N\xi_2 \frac{1}{x_2})! / (N\xi_1 \frac{1}{x_1})! (N\xi_2 \frac{1}{x_2})!$, introduced in the complete partition function is due to the random mixing of the solid-like molecules, as we assumed.

The solid-like parts of the partition function for the two components are given by;

$$f_{1s} = \frac{e^{E_{s1}/RT}}{(1 - e^{-\theta_1/T})^6} \left\{ 1 + n_1(x_1 - 1)e^{-\frac{\phi_{11}n_1}{n_1(x_1-1)RT}} \right\} \frac{1}{\prod_{D6h}} \dots\dots\dots(6)$$

$$f_{2s} = \frac{e^{E_{s2}/RT}}{(1 - e^{-\theta_2/T})^6} \left\{ 1 + n_2(x_2 - 1)e^{-\frac{\phi_{22}n_2}{n_2(x_2-1)RT}} \right\} \frac{1}{\prod_{C2h}} \dots\dots\dots(7)$$

where the subscripts 1 and 2 indicate the component one and two, respectively.

The gas-like parts of the partition function for the two components are given by,

$$f_{1g}^{\frac{N_{21}(1-\frac{1}{x_1})}{N_{21}}} = \left[\frac{(2\pi m_1 RT)^{3/2}}{h^3} \frac{e^{(V + V_{s1}^\circ - V_s)}}{N_{21}^{\xi_1}} \right] \frac{1}{\left[N_{21} \left(1 - \frac{1}{x_1} \right) \right]^!} \left\{ \frac{\sqrt{\pi}(8\pi^2 RT)^{3/2} (I_A' I_B' I_C')^{1/2}}{12h^3} \frac{1}{\prod_{D6h}} \right\}^{N_{21}(1-\frac{1}{x_1})} \dots\dots(8)$$

$$f_{2g}^{\frac{N_{22}(1-\frac{1}{x_2})}{N_{22}}} = \left[\frac{(2\pi m_2 RT)^{3/2}}{h^3} \frac{e^{(V + V_{s2}^\circ - V_s)}}{N_{22}^{\xi_2}} \right] \frac{1}{\left[N_{22} \left(1 - \frac{1}{x_2} \right) \right]^!} \left\{ \frac{\sqrt{\pi}(8\pi^2 RT)^{3/2} (I_A'' I_B'' I_C'')^{1/2}}{2h^3} \frac{1}{\prod_{C2h}} \right\}^{N_{22}(1-\frac{1}{x_2})} \dots\dots\dots(9)$$

The heat of sublimation of the solid-like molecules of the components in the mixture are determined by using following equations;

$$E_{s1} = \frac{1}{2} \phi_{11} n_1 \xi_1 + \frac{1}{2} \phi_{12} n_1 \xi_2$$

$$= E_{s1}^\circ \xi_1 + \frac{1}{2} \phi_{12} n_1 \xi_2 \dots\dots\dots(10)$$

where ϕ_{11} and ϕ_{12} are molar binding energies between the molecules of the component one and

that between the molecules of the two different types, respectively. Likewise for the second component;

$$E_{s2} = E_{s2}^\circ \xi_2 + \frac{1}{2} \phi_{12} n_2 \xi_1 \dots\dots\dots(11)$$

The mean heat of sublimation of the solid-like molecules in the mixture can be given by;

$$E_s = E_{s1} \xi_1 + E_{s2} \xi_2$$

$$= E_{s1}^\circ \xi_1^2 + E_{s2}^\circ \xi_2^2 + \frac{1}{2} \phi_{12} \xi_1 \xi_2 (n_1 + n_2) \dots\dots(12)$$

The equation (12) is obtained by introducing equations (10) and (11). On the other hand the mean heat of sublimation can be equated as;

$$E_s = E_{s1}^\circ \xi_1 + E_{s2}^\circ \xi_2 + \Delta H_{mix} \dots\dots\dots(13)$$

since the total energy of the system should be conserved. From the knowledge of the heat of mixing, ΔH_{mix} , ϕ_{12} can be obtained by combining equations (12) and (13). For the benzene-ethylenechloride system, the heat of mixing is zero throughout the temperature range under consideration,¹⁰ and $\frac{1}{2} \phi_{12}$ is found to be 819.79 cal/mole. E_s and V_s for the system are also calculated, and given in Table I.

The number of average vacant holes around a molecule can be given by;

$$x_1 - 1 = (V - V_s) / V_{s1}^\circ \dots\dots\dots(14)$$

$$x_2 - 1 = (V - V_s) / V_{s2}^\circ \dots\dots\dots(15)$$

The relation between x_1 and x_2 can be obtained from the above two equations;

$$x_2 - 1 = (x_1 - 1) V_{s1}^\circ / V_{s2}^\circ \dots\dots\dots(16)$$

Calculations

The partition function is related to the Helmholtz free energy as follows;

$$A = -RT \ln F(T, V, \xi_1, \xi_2) \dots\dots\dots(17)$$

Table I Calculated Values of E_s and V_s .

ξ_1	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
E_{s1} cal/mole	9364.3	9394.5	9424.7	9454.9	9485.1	9515.3	9545.5	9575.7	9605.9
E_{s2} cal/mole	9436.1	9466.3	9496.5	9526.7	9556.9	9587.0	9617.2	9647.4	9677.6
V_s cc	74.182	75.143	76.103	77.064	78.024	78.984	79.945	80.905	81.866

Since all the parameters appearing in the complete partition function is known, the thermodynamic properties of the system can be derived from equation (17). The calculations are made at 293.15°, 323.14° and 357.15° K.

1) **Total Vapor Pressures and Molar Volumes:** The Helmholtz free energy versus the molar volume is plotted for different values of the

molar volumes of the system. Then, the slope of the common tangential line between the liquidous portion and gaseous portion gives the total vapor pressure of the system in equilibrium with its vapor, like in the single component system.²⁾ And the molar volume of the liquid is obtained from the tangential point at the liquidous portion. The calculated values are given in the fifth and

Table III Total and Partial Pressures at 293.15° K.

ξ_1	M. V.	P_1^{cal}	P_2^{cal}	P_{total}^{cal}	P_1^*	P_2^*	$P_1^{cal} + P_2^{cal}$	$P_1^* + P_2^*$
0.0	77.40 cc	atm 0	atm 0.0881	atm 0.0881	atm 0	atm 0.0881	atm 0.0881	atm 0.881
0.1	78.49	0.0098	0.0793	0.0890	0.0099	0.0793	0.0891	0.0891
0.2	79.53	0.0196	0.0705	0.0900	0.0197	0.0705	0.0902	0.0902
0.3	80.66	0.0294	0.619	0.0910	0.0295	0.0617	0.0913	0.0912
0.4	81.78	0.0392	0.0532	0.0922	0.0394	0.0529	0.0923	0.0923
0.5	82.91	0.0490	0.0444	0.0933	0.0492	0.0441	0.0934	0.0933
0.6	84.04	0.0588	0.0356	0.0944	0.0591	0.0352	0.0944	0.0943
0.7	85.16	0.0687	0.0268	0.0954	0.0689	0.0264	0.0954	0.0954
0.8	86.29	0.0785	0.0179	0.0964	0.0788	0.0176	0.0964	0.0964
0.9	87.41	0.0884	0.0089	0.0975	0.0886	0.0088	0.0973	0.0974
1.0	88.67	0.0983	0	0.0985	0.0985	0	0.0985	0.0985

* Calculated values from the individual partition functions of each component.

Table IV Total and Partial Pressures at 323.14° K.

ξ_1	M. V.	P_1^{cal}	P_2^{cal}	P_{total}^{cal}	P_1^*	P_2^*	$P_1^{cal} + P_2^{cal}$	$P_1^* + P_2^*$
0.0	79.56 cc	atm 0	atm 0.3136	atm 0.3136	atm 0	atm 0.3136	atm 0.3136	atm 0.3136
0.1	80.81	0.0350	0.2832	0.3177	0.0353	0.2822	0.3182	0.3175
0.2	81.85	0.0703	0.2517	0.3218	0.0706	0.2509	0.3219	0.3215
0.3	82.98	0.1055	0.2204	0.3260	0.1059	0.2195	0.3259	0.3254
0.4	84.19	0.1405	0.1896	0.3300	0.1412	0.1882	0.3300	0.3294
0.5	85.40	0.1755	0.1585	0.3330	0.1765	0.1568	0.3341	0.3330
0.6	86.60	0.2107	0.1273	0.3380	0.2118	0.1254	0.3380	0.3372
0.7	87.81	0.2460	0.0959	0.3420	0.2471	0.0941	0.3418	0.3412
0.8	88.94	0.2814	0.0639	0.3454	0.2824	0.0627	0.3452	0.3451
0.9	90.23	0.3169	0.0322	0.3492	0.3177	0.0314	0.3491	0.3491
1.0	91.52	0.3530	0	0.3530	0.3530	0	0.3530	0.3530

* Calculated values from the individual partition functions of each component.

Table V Total and Partial Pressures at 357.15°K.

ξ_1	<i>M. V.</i>	P_1^{cal}	P_2^{cal}	P^{cal}_{total}	P_1^*	P_2^*	$P_1^{cal} + P_2^{cal}$	$P_1^* + P_2^*$
	cc	atm	atm	atm	atm	atm	atm	atm
0.0	82.45	0	0.9814	0.9814	0	0.9814	0.9814	0.9814
0.1	83.63	0.1106	0.8840	0.995	0.1111	0.8832	0.995	0.994
0.2	84.75	0.2215	0.7865	1.009	0.2221	0.7851	1.008	1.007
0.3	86.04	0.3316	0.6906	1.022	0.3332	0.6870	1.022	1.020
0.4	87.25	0.4422	0.5930	1.035	0.4442	0.5888	1.035	1.033
0.5	88.54	0.5524	0.4962	1.048	0.5553	0.4907	1.048	1.045
0.6	89.84	0.6629	0.3987	1.061	0.6663	0.3926	1.062	1.059
0.7	92.13	0.7738	0.3008	1.074	0.7774	0.2944	1.075	1.072
0.8	92.42	0.8852	0.2017	1.086	0.8884	0.1963	1.089	1.085
0.9	93.79	0.9974	0.1013	1.098	0.9995	0.0981	1.099	1.098
1.0	95.08	1.111	0	1.111	1.111	0	1.111	1.111

* Calculated values from the individual partition functions of each component.

second columns of Table III, IV, and V.

2) **Partial Vapor Pressures:** The partial pressures of the component one are calculated from the relation;

$$\mu_1^* = \mu_1^\circ + RT \ln \frac{p_1}{p_1^\circ} \dots \dots \dots (18)$$

The chemical potential μ_1^* and μ_1° for the component one of the system and the pure liquid are deduced by the thermodynamic relation;

$$\mu_i = \left(\frac{\partial A}{\partial N_i} \right)_{T, V, N_{j \neq i}} \dots \dots \dots (19)$$

The partial pressures of the second component are also calculated in the same manner. The results are given in the third and fourth columns of Table III, IV, and V.

3) **Entropies of Mixing:** The entropies of mixing, the difference between the total entropy of the system and the sum of the entropies of the two components at the pure state, are calculated. The ideal mixing entropies are also calculated from the following equation;

$$\frac{\Delta S}{R} = -\xi_1 \ln \xi_1 - \xi_2 \ln \xi_2 \dots \dots \dots (20)$$

They are compared as shown in Table VI.

Table VI Mixing Entropy.

ξ_1	ΔS_{ideal} (e. u.)	ΔS (e. u.) (calculated from the complete partition function)		
		296.15°K	323.14°K	357.15°K
0.1	0.646	0.642	0.667	0.631
0.2	0.994	0.968	0.978	0.953
0.3	1.214	1.192	1.183	1.183
0.4	1.337	1.319	1.312	1.297
0.5	1.378	1.361	1.356	1.345
0.6	1.337	1.323	1.319	1.311
0.7	1.214	1.200	1.197	1.192
0.8	0.994	0.980	0.958	0.976
0.9	0.646	0.631	0.629	0.646

Summary

The sixth and seventh columns of Table III, IV, and V are the partial pressures, calculated from the vapor pressures of the components at the pure state using the Raoult's law.

Comparing the third and sixth columns, and also the fourth and seventh columns, the calculations from the individual partition functions and those from the complete partition function agree very well. However the theoretical values deviate

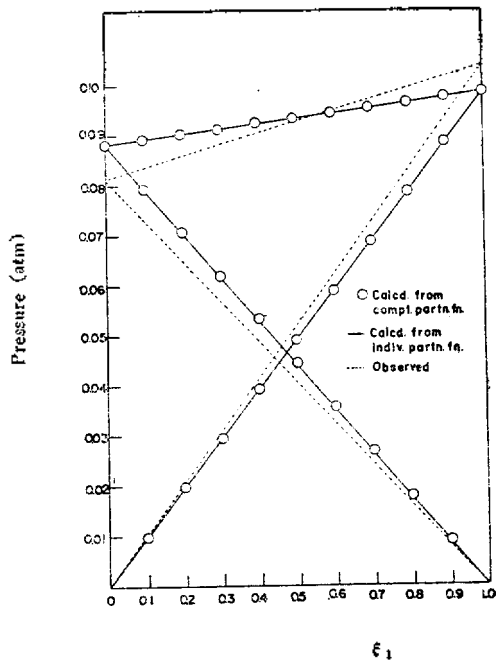


Fig. 1 Total and partial pressures at 293.15°K.

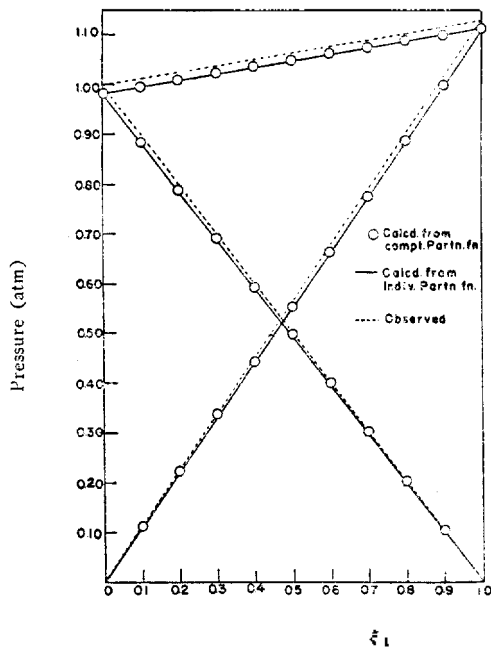


Fig. 3 Total and partial pressures at 357.15°K.

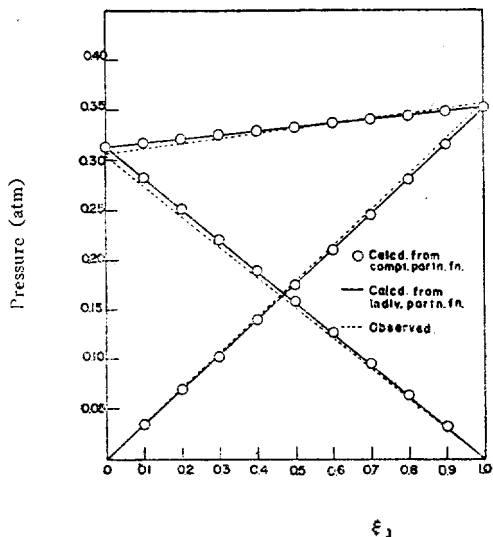


Fig. 2 Total and partial pressures at 323.14°K.

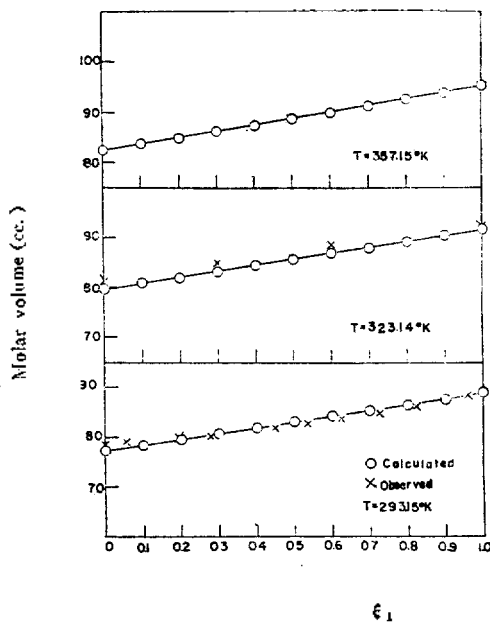


Fig. 4 Molar volume.

from the experimentally observed values^{11,12)} to some extent. From the above results, however, the better agreement between the experimentally observed values and the calculated values from the complete partition function can be expected, if the better partition functions for the individual

components are available. The total and partial pressures are graphically represented in Figure 1, 2, and 3.

The molar volumes are also plotted in Figure 4 to compare with the experimental values.¹³⁾

The calculated mixing entropies are compared with the ideal mixing entropies. The observed values of mixing entropies are not available in literature.

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