

이성분 용액의 액체-증기 계면에 대한 통계 열역학적 연구

서울대학교 교양과정부 화학과 박형석

The Statistical Thermodynamic Approach to the
Liquid-Vapor Interface of Binary Solution

Hyungsuk Pak

Department of Chemistry, College of General Studies, Seoul National
University, Seoul, Korea.

(Received Feb. 18, 1971)

요 약 액체구조의 천이상태이론을 이성분용액의 액체-증기 계면에 적용하여, $C_6H_{12}-C_6H_6$, $CCl_4-C_6H_6$, $CHCl_3-C_6H_6$, $CHCl_3-CCl_4$, CCl_4-CS_2 계의 표면장력, 표면흡착량, 표면에서의 활동도 계수들을 계산하였다.

Abstract A method of theoretical calculation of the thermodynamic properties for liquid-vapor interface of binary solution is developed according to the transient state theory of significant liquid structure. The surface tensions, the adsorbed amounts at the liquid-vapor interface and the activity coefficients of the components for the solutions of $C_6H_{12}-C_6H_6$, $CCl_4-C_6H_6$, $CHCl_3-C_6H_6$, $CHCl_3-CCl_4$ and CCl_4-CS_2 are calculated through the full ranges of the compositions.

I. Introduction.

There are several theoretical approaches¹⁻⁸ to the liquid-vapor interface of binary solution by quasi-lattice or cell model for the liquid state. Recently, S. W. Kim et al⁹ have applied Eyring's significant structure theory of liquids¹⁰ to the interface and have calculated the surface tension by using the simplified Eckert-Prausnitz equation⁶ in obtaining surface compositions and by assuming that the ratio of the activity coefficients for the two components is unity.

H. Pak, W. Ahn and S. Chang¹¹ have developed the transient state theory of significant liquid structure by considering three kinds of degrees of freedom for the liquid state. The theory of liquids has been applied to various kinds of liquids, including binary solution, with success¹¹⁻²¹ and it is also applied to the physical adsorption of gases on solid surfaces

by S. Chang and H. Pak²².

In application of the theory of liquids to the interface of solution, it is considered that the transition region consists of multimolecular layers as shown in the liquid-vapor interface of single liquids by S. Chang et al²³.

II. Theory.

According to the transient state theory of significant liquid structure the degrees of freedom for the liquid state are partitioned into gas-like, transient and solid-like. As $N(V-V_s)/V_s$ vacancies of molecular size are distributed at random among N molecules, $(N(V-V_s)/V_s)/(N+N(V-V_s)/V_s)=(V-V_s)/V$ fraction of the molecules may have an opportunity to jump into the vacancies as if they were in a gaseous state having a volume of $(V-V_s)$, where V and V_s are the volumes of N molecules in the liquid state and in the solid state, respectively.

Of the remaining molecules, NV_s/V , the ones around the vacancies gain strain energy, $\epsilon = a/(n(V - V_s)/V_s)$, n being the coordination number of the molecule, due to the structural distortion and have a transient degrees of freedom. And the others are restrained to an equilibrium position much as if they were in a solid state. From this model, the partition function for the liquid state is given as follows:

$$Q(N, V, T) = \left[\frac{e^{E_s/RT} b_s}{(1 - e^{-\theta_s/RT})^3} \left\{ 1 + n \left(\frac{V - V_s}{V_s} \right) \left(\frac{1 - e^{-\theta_s/RT}}{1 - e^{-\theta_t/RT}} \right)^3 \frac{b_t}{b_s} e^{-\epsilon/RT} \right\} \right]^{\frac{V - N}{V}} \cdot \left[\frac{(2\pi m_i k T)^{3/2}}{h^3} (V - V_s) b_{si} \right]^{\frac{V - N_s}{V}} \cdot \frac{1}{\left[\left(\frac{V - V_s}{V} \right)! \right]} \quad (1)$$

where, E_s is the ground state energy of the solid-like molecule, θ 's are Einstein characteristic temperatures and b 's are the product of the internal partition functions and the partition functions for the molecular rotations in the respective state, and the subscripts s , t and g stand for the solid-like, the transient and the gas-like, respectively.

This theory of liquid is extended to the binary liquid solution which is composed of N_1 and N_2 molecules of components 1 and 2, respectively. If it is assumed that the two components are mixed at random and that the size of the vacant site introduced in the solution is equal to V_s/N , the number of gas-like molecules becomes $N(V - V_s)/V$ and the remaining molecules, NV_s/V , are partitioned into the solid-like and the transient state. Here, $N = N_1 + N_2$ and V_s is given as

$$V_s = N_1 v_{s1} + N_2 v_{s2} \quad (2),$$

where v_{s1} and v_{s2} are the molecular volumes

of respective components in the solid state. Then, the partition function for the binary liquid solution becomes

$$Q(N_1, N_2, V, T) = \frac{\left[\frac{V_s}{V} (N_1 + N_2) \right]!}{\left[\frac{V_s}{V} N_1 \right]! \left[\frac{V_s}{V} N_2 \right]!} e^{\frac{E_s}{RT} \frac{V_s}{V}} \cdot \frac{1}{\prod_i} \left[\frac{b_{si}}{(1 - e^{-\theta_{si}/RT})^3} \left\{ 1 + n_i \left(\frac{V - V_s}{V_s} \right) \left(\frac{1 - e^{-\theta_{si}/RT}}{1 - e^{-\theta_{ti}/RT}} \right)^3 \frac{b_{ti}}{b_{si}} e^{-\frac{\epsilon_i}{RT}} \right\} \right]^{\frac{V - N_i}{V}} \cdot \left[\frac{(2\pi m_i k T)^{3/2}}{h^3} (V - V_s) b_{si} \right]^{\frac{V - N_{si}}{V}} \cdot \frac{1}{\left[\left(\frac{V - V_s}{V} \right)! \right]} \quad (3)$$

In equation (3) E_s is taken as follows:

$$\left(E_s = \frac{1}{2} \phi_{11} n_{11} \frac{N_1}{N} + \frac{1}{2} \phi_{12} n_{12} \frac{N_2}{N} \right) N_1 + \left(\frac{1}{2} \phi_{22} n_{22} \frac{N_2}{N} + \frac{1}{2} \phi_{21} n_{21} \frac{N_1}{N} \right) N_2 \quad (4)$$

where ϕ_{ij} is the interaction energy between the molecules of i and j , and n_{ij} is the maximum number of molecules of j that can be neighbored to a molecule of i , if it is assumed that

$$\frac{1}{2} (\phi_{12} n_{12} + \phi_{21} n_{21}) = (\phi_{11} n_{12} \cdot \phi_{22} n_{21})^{1/2} \quad (5)$$

then,

$$E_s = \frac{1}{4} (\phi_{12} n_{12} + \phi_{21} n_{21}) N = (E_{s1} \cdot E_{s2})^{1/2} \left(\frac{n_{12} n_{21}}{n_{11} n_{22}} \right) \quad (6)$$

where $E_{si} = \frac{1}{2} \phi_{ii} n_{ii} N$ is the ground state energy for the component i in pure liquid state. By considering the relative size of the molecules it can be shown that

$$n_{ij} = n_{ii} \left(\frac{2v_{ii}^{1/3}}{v_{ij}^{1/3} + v_{ii}^{1/3}} \right)^2 \quad (7)$$

if it is assumed that the molecules are spherically symmetric. Then, can be found as follows:

$$E_m = (E_{s1} \cdot E_{s2})^{1/2} \left(\frac{4v_{s1}^{1/3} + v_{s2}^{1/3}}{(v_{s1}^{1/3} + v_{s2}^{1/3})^2} \right) \quad (8)$$

$$V_i = N_0 \left(\frac{\partial V}{\partial N_i} \right)_{N_1, T, P} = -N_0 \left(\frac{\partial P}{\partial N_i} \right)_{N_1, T, V} / \left(\frac{\partial P}{\partial V} \right)_{N_1, N_2, T} \quad (14)$$

and

$$E_s = x_1^2 E_{s1} + 2x_1 x_2 E_m + x_2^2 E_{s2} \quad (9)$$

where x_1 and x_2 are the mole fractions of the components 1 and 2, respectively.

By introducing equation (3) into the statistical thermodynamic relation

$$A = -kT \ln Q(N_1, N_2, V, T) \quad (10)$$

the chemical potential (partial molar Gibbs free energy) for component i and the total vapor pressure are given as follows:

$$\mu_i = -RT \left(\frac{\partial \ln Q}{\partial N_i} \right)_{N_1, V, T} \quad (11)$$

$$P = -kT \left(\frac{\partial \ln Q}{\partial V} \right)_{N_1, N_2, T} \quad (12)$$

If the vapor is assumed to be an ideal gas, the partial pressure P_i for the component i is given by

$$P_i = \exp \left(\frac{\mu_i - \mu_i^*(g)}{RT} \right) \quad (13)$$

where $\mu_i^*(g)$ is the chemical potential for the pure component i in gaseous state. By introducing the relation $P_1 + P_2 = P$, the equations (11), (12) and (13) can be solved for μ_i , P and V simultaneously. And then, all the other thermodynamic properties for the liquid solution can easily be found from the partition function.

From equation (12) the partial molar volumes

where N_0 is Avogadro's number.

In application of the theory of solution to the interfacial region, the ground state energy E_s has to be corrected since the molecules in the region is in different energy state from those in the bulk liquid solution. By analogy with the theory of surface tension for the pure liquid which was proposed by S. Chang et al²³, the ground state energy for the m -th interfacial layer, $E_s(m)$, is given as follows:

$$E_s(m) = E_s \left(\frac{3}{12} \frac{\rho_{m+1}}{\rho_m} + \frac{6}{12} \frac{\rho_m}{\rho_m} + \frac{3}{12} \frac{\rho_{m-1}}{\rho_m} \right) \quad (15)$$

where ρ_m is the number density of the m -th interfacial layer which is inversely proportional to the volume of the m -th layer. For the top surface layer, however, the following relation is used:

$$E_s(1) = E_s \left(\frac{3}{12} \frac{\rho_2}{\rho_1} + \frac{6}{12} \frac{\rho_1}{\rho_1} + \frac{3}{12} \frac{PV(1)}{RT} \right) \quad (16)$$

where $V(1)$ is the molar volume of the top layer. Introducing equations (16) and (15) into equation (3) various thermodynamic properties for the interfacial layers can be calculated by the similar iteration method of S. Chang et al²³ only if the compositions of the layers, which are all in equilibrium with the bulk liquid solution, are available.

It can be shown that the chemical potentials of the components in the m -th interfacial layer, $\mu_1(m)$ and $\mu_2(m)$, are related to those of the components in the bulk liquid solution, μ_1 and

μ_2 , by the equation

$$\frac{\mu_1(m) - \mu_1}{\alpha_1(m)} = \frac{\mu_2(m) - \mu_2}{\alpha_2(m)} = \gamma(m) \quad (17)$$

where $\alpha_1(m)$ and $\alpha_2(m)$ are the corresponding partial partial molar areas in the m -th layer and $\gamma(m)$ is the excess Gibbs free energy per unit area of the layer.

The partial molar areas can be obtained by dividing the partial molar volumes of the layers, which are given by equation (14), with the corresponding layer thickness, $d(m)$. The latter is given by

$$d(m) = 0.9165 (v_{s1}x_1(m) + v_{s2}x_2(m))^{1/3} \quad (18)$$

where $x_1(m)$ and $x_2(m)$ are the mole fractions of the m -th layer, if it is assumed that the most dense molecular planes appear in the interfacial layers.

The equation (17) is rearranged to give

$$\frac{\mu_1(m) - \mu_1}{\mu_2(m) - \mu_2} = \frac{\alpha_1(m)}{\alpha_2(m)} \quad (19)$$

The volume and the compositions for the interfacial layer can be found by solving equations (12) and (19) simultaneously at a given temperature. Then, all the thermodynamic properties for the layer are obtainable.

The Gibbs equation for the m -th interfacial layer of the binary solution is

$$-d\gamma(m) = \Gamma_1(m)d\mu_1 + \Gamma_2(m)d\mu_2 \quad (20)$$

where $\Gamma_1(m)$ and $\Gamma_2(m)$ are the concentrations (moles per unit area) of the m -th layer for the components 1 and 2, respectively: whence, from the Gibbs-Duhem equation $x_1d\mu_1 + x_2d\mu_2 = 0$, the following equation is obtained:

$$\begin{aligned} x_2 \frac{d\gamma(m)}{d\mu_1} &= \Gamma_2(m) - x_2(\Gamma_1(m) + \Gamma_2(m)) \\ &\equiv \Gamma_2^{(N)}(m) \end{aligned} \quad (21)$$

The latter is the excess of component 2 in the m -th layer of unit area compared with the amount present in the quantity of bulk liquid solution which contains the same total number of moles of all species. It can be shown that

$$\begin{aligned} \Gamma_2^{(N)}(m) &= \frac{x_2(m) - x_2}{\alpha(m)} \\ &= -\frac{x_1(m) - x_1}{\alpha(m)} = -\Gamma_1^{(N)}(m) \end{aligned} \quad (22)$$

where $\alpha(m)$ is the molar area of the m -th layer which is equal to $\alpha_1(m) \cdot x_1(m) + \alpha_2(m) \cdot x_2(m)$. The total surface excess of component i is the sum of the excesses of all the interfacial layers, that is,

$$\Gamma_i^{(N)} = \sum_m \Gamma_i^{(N)}(m) = \sum_m (x_i(m) - x_i) / \alpha(m) \quad (23)$$

The interfacial tension (surface tension) of the solution is the sum of the excess Gibbs free energies per unit area of all the interfacial layers as follows:

$$\gamma = \sum_m \gamma(m) \quad (24)$$

The activity coefficient of component i in the m -th layer, $f_i(m)$, is related to the chemical potentials $\mu_i(m)$ and $\mu_i^*(m)$ as follows:

$$\mu_i(m) = \mu_i^*(m) + RT \ln x_i(m) + RT \ln f_i(m) \quad (25)$$

where $\mu_i^*(m)$ is the chemical potential for the m -th interfacial layer of component i in the pure liquid state.

III. Results.

The calculated values of the vapor pressures,

the partial pressures, the molar volumes and the partial molar volumes for the bulk liquid solutions of $C_6H_{12}(1)-C_6H_6(2)$ at 293.15°K, $CCl_4(1)-C_6H_6(2)$ at 313.15°K, $CHCl_3(1)-C_6H_6(2)$ at 298.15°K, $CHCl_3(1)-CCl_4(2)$ at 291.15°K and $CCl_4(1)-CS_2(2)$ at 305.05°K through the full ranges of the compositions are listed in the table I.

The calculated values of the surface tensions and the partial molar volumes of the components 1 and 2 for each interfacial layer for the above

five couples of solution are listed in the table II.

The adsorbed amounts of component 1 at each interfacial layer, $\Gamma_1^{(m)}$ (m), and the sums, $\Gamma_1^{(N)}$, for the above five couples of solution are calculated according to the equations (22) and (23) and are listed in the table III.

The activity coefficients of the components 1 and 2 in each interfacial layer, $f_i(m)$, for the above five couples of solution are calculated according to the equation (25) and are listed in the table IV.

Table I. Vapor Pressure, Partial Pressures, Molar Volume and Partial Molar Volumes for Bulk Liquid Solution.

x_1	$P(\text{atm})$	$P_1(\text{atm})$	$P_2(\text{atm})$	$V(\text{cc})$	$V_1(\text{cc})$	$V_2(\text{cc})$
$C_6H_{12}(1)-C_6H_6(2)$						
0.0	0.09814	0.00000	0.09814	88.525	...	88.525
0.1	0.10045	0.01230	0.08814	90.882	111.885	88.548
0.2	0.10228	0.02379	0.07849	93.191	111.463	88.623
0.3	0.10367	0.03458	0.06909	95.448	111.045	88.763
0.4	0.10465	0.04482	0.05983	97.645	110.635	88.985
0.5	0.10525	0.05462	0.05063	99.775	110.237	89.312
0.6	0.10547	0.06411	0.04135	101.826	109.859	89.777
0.7	0.10529	0.07342	0.03186	103.786	109.510	90.428
0.8	0.10468	0.08268	0.02199	105.635	109.209	91.342
0.9	0.10356	0.09207	0.01148	107.349	108.983	92.639
1.0	0.10179	0.10179	0.00000	108.889	108.889	...
$CCl_4(1)-C_6H_6(2)$						
0.0	0.23741	0.00000	0.23741	90.271	...	90.271
0.1	0.24516	0.03165	0.21351	91.246	99.878	90.286
0.2	0.25196	0.06180	0.19015	92.186	99.601	90.335
0.3	0.25788	0.09068	0.16719	93.098	99.335	90.424
0.4	0.26298	0.11854	0.14444	93.969	99.082	90.561
0.5	0.26732	0.14559	0.12172	94.800	98.847	90.753
0.6	0.27092	0.17208	0.09883	95.587	98.636	91.012
0.7	0.27379	0.19825	0.07554	96.324	98.455	91.349
0.8	0.27592	0.22436	0.05155	97.006	98.313	91.777
0.9	0.27724	0.25071	0.02652	97.629	98.221	92.304
1.0	0.27768	0.27768	0.00000	98.188	98.188	...
$CHCl_3(1)-C_6H_6(2)$						
0.0	0.12401	0.00000	0.12401	88.954	...	88.954
0.1	0.13874	0.02686	0.11187	88.130	80.640	88.963
0.2	0.15316	0.05338	0.09978	87.290	80.504	88.986
0.3	0.16736	0.07967	0.08768	86.434	80.394	89.023
0.4	0.18138	0.10583	0.07554	85.564	80.305	89.070

0.5	0.19526	0.13192	0.06333	84.681	80.235	89.127
0.6	0.20906	0.15805	0.05101	83.786	80.182	89.192
0.7	0.22282	0.18426	0.03855	82.879	80.142	89.265
0.8	0.23656	0.21064	0.02592	81.961	80.115	89.345
0.9	0.25033	0.23725	0.01307	81.033	80.100	89.432
1.0	0.26416	0.26416	0.00000	80.095	80.095	...
CHCl₃(1)-CCl₄(2)						
0.0	0.10788	0.00000	0.10788	95.990	...	95.990
0.1	0.12187	0.02408	0.09778	94.940	84.475	96.103
0.2	0.13326	0.04506	0.08820	93.681	82.900	96.376
0.3	0.14310	0.06436	0.07873	92.258	81.805	96.737
0.4	0.15191	0.08277	0.06913	90.703	81.034	97.149
0.5	0.16001	0.10078	0.05922	89.041	80.487	97.594
0.6	0.16758	0.11872	0.04885	87.286	80.102	98.062
0.7	0.17476	0.13687	0.03788	85.452	79.839	98.548
0.8	0.18161	0.15543	0.02618	83.547	79.672	99.048
0.9	0.18821	0.17460	0.01360	81.579	79.581	99.561
1.0	0.19456	0.19456	0.00000	79.553	79.553	...
CCl₄(1)-CS₂(2)						
0.0	0.66817	0.00000	0.66817	60.882	...	60.882
0.1	0.62555	0.03103	0.59451	65.267	104.243	60.937
0.2	0.58470	0.05768	0.52701	69.541	103.250	61.113
0.3	0.54507	0.08082	0.46425	73.691	102.287	61.436
0.4	0.50605	0.10117	0.40488	77.707	101.363	61.936
0.5	0.46687	0.11938	0.34749	81.571	100.484	62.658
0.6	0.42653	0.13601	0.29051	85.265	99.658	63.674
0.7	0.38354	0.15163	0.23190	88.757	98.892	65.107
0.8	0.33552	0.16683	0.16869	92.003	98.204	67.197
0.9	0.27791	0.18237	0.09554	94.925	97.640	70.484
1.0	0.19966	0.19966	0.00000	97.360	97.360	...

Table II. Surface Tension and Partial Molar Volumes of Interfacial Layers.

x_1	γ (dyne/cm)	$V_1(1)$ (cc)	$V_2(1)$ (cc)	$V_1(2)$ (cc)	$V_2(2)$ (cc)	$V_1(3)$ (cc)	$V_2(3)$ (cc)
C₆H₁₂(1)-C₆H₆(2)							
0.0	41.005	...	101.098	...	89.425	...	88.530
0.1	39.427	126.425	101.478	112.928	89.421	111.926	88.612
0.2	38.146	125.734	102.011	112.443	89.495	111.543	88.684
0.3	37.091	125.264	102.567	111.993	89.650	111.110	88.823
0.4	36.207	124.933	103.111	111.578	89.896	110.698	89.045
0.5	35.452	124.685	103.640	111.198	90.247	110.301	89.374
0.6	34.800	124.487	104.158	110.857	90.724	109.926	89.840
0.7	34.229	124.323	104.676	110.560	91.360	109.584	90.492
0.8	33.725	124.183	105.209	110.319	92.203	109.292	91.403
0.9	33.278	124.061	105.776	110.152	93.330	109.078	92.686
1.0	32.880	123.957	...	110.095	...	108.996	...

CCl₄(1)-C₆H₆(2)							
0.0	38.382	...	105.316	...	91.450	...	90.871
0.1	37.543	115.029	105.500	101.077	91.448	99.977	90.382
0.2	36.807	114.547	105.771	100.759	91.491	99.694	90.428
0.3	36.157	114.182	106.096	100.464	91.581	99.424	90.516
0.4	35.579	113.900	106.458	100.194	91.724	99.169	90.651
0.5	35.064	113.680	106.849	99.951	91.925	98.933	90.843
0.6	34.603	113.506	107.264	99.739	92.194	98.721	91.103
0.7	34.188	113.373	107.711	99.561	92.538	98.540	91.441
0.8	33.816	113.273	108.196	99.424	92.971	98.400	91.870
0.9	33.480	113.207	108.731	99.335	93.505	98.308	92.399
1.0	33.180	113.178	...	99.303	...	98.277	...
CHCl₃(1)-C₆H₆(2)							
0.0	40.357	...	102.090	...	89.913	...	89.029
0.1	40.213	94.286	102.052	81.546	89.930	80.710	89.038
0.2	40.079	94.158	102.022	81.430	89.961	80.575	89.063
0.3	39.955	94.039	102.001	81.336	90.004	80.467	89.100
0.4	39.839	93.930	101.987	81.262	90.057	80.380	89.148
0.5	39.732	93.829	101.982	81.205	90.120	80.312	89.206
0.6	39.632	93.734	101.983	81.163	90.192	80.259	89.272
0.7	39.539	93.646	101.991	81.134	90.272	80.221	89.346
0.8	39.453	93.564	102.006	81.117	90.351	80.196	89.428
0.9	39.374	93.489	102.030	81.112	90.458	80.182	89.516
1.0	39.300	93.418	...	81.117	...	80.179	...
CHCl₃(1)-CCl₄(2)							
0.0	35.747	...	108.169	...	96.803	...	96.048
0.1	35.807	98.143	108.241	85.272	96.905	84.528	96.157
0.2	35.960	97.124	108.384	83.780	97.150	82.956	96.425
0.3	36.186	96.290	108.571	82.721	97.478	81.860	96.782
0.4	36.482	95.555	108.800	81.953	97.863	81.089	97.191
0.5	36.851	94.875	109.077	81.392	98.293	80.541	97.635
0.6	37.301	94.227	109.421	80.987	98.764	80.156	98.105
0.7	37.847	93.598	109.858	80.708	99.274	79.895	98.595
0.8	38.508	92.990	110.445	80.534	99.826	79.730	99.102
0.9	39.309	92.428	111.280	80.456	100.425	79.645	99.624
1.0	40.282	91.988	...	80.469	...	79.625	...
CCl₄(1)-CS₂(2)							
0.0	41.433	...	71.705	...	61.761	...	60.959
0.1	38.936	117.379	73.223	105.203	61.767	104.316	60.999
0.2	37.308	115.442	74.831	103.983	61.988	103.298	61.170
0.3	36.195	114.300	76.276	102.909	62.399	102.322	61.491
0.4	35.404	113.512	77.595	101.953	63.007	101.392	61.992
0.5	34.835	112.913	78.845	101.098	63.836	100.513	62.718
0.6	34.428	112.429	80.088	100.336	64.931	99.690	63.740
0.7	34.150	112.019	81.404	99.659	66.388	98.933	65.180
0.8	33.989	111.667	82.918	99.069	68.402	98.256	67.273
0.9	33.960	111.376	84.889	98.590	71.435	97.706	70.550
1.0	34.138	111.225	...	98.347	...	97.435	...

Table III. Absorbed Amounts(in $\mu\text{moles}/\text{m}^2$) at Liquid-Vapor Interface of Solution.

x_1	$\Gamma_1^{(N)}(1)$	$\Gamma_1^{(N)}(2)$	$\Gamma_1^{(N)}(3)$	$\Gamma_1^{(N)}(4)$	$\Gamma_1^{(N)}$
$\text{C}_6\text{H}_{12}(1)-\text{C}_6\text{H}_6(2)$					
0.0	0.00000	0.00000	0.00000	0.00000	0.00000
0.1	0.68015	0.07019	0.00520	0.00038	0.75593
0.2	0.94232	0.11368	0.00824	0.00059	1.06485
0.3	1.01101	0.13775	0.00980	0.00067	1.15923
0.4	0.97330	0.14606	0.01033	0.00069	1.13039
0.5	0.87126	0.14107	0.01003	0.00066	1.02305
0.6	0.72853	0.12486	0.00908	0.00061	0.86310
0.7	0.56007	0.09966	0.00753	0.00053	0.66781
0.8	0.37655	0.06805	0.00542	0.00040	0.45044
0.9	0.18688	0.03336	0.00281	0.00022	0.00328
1.0	0.00000	0.00000	0.00000	0.00000	0.00000
$\text{CCl}_4(1)-\text{C}_6\text{H}_6(2)$					
0.0	0.00000	0.00000	0.00000	0.00000	0.00000
0.1	0.29393	0.04492	0.00389	0.00032	0.34307
0.2	0.45870	0.07559	0.00649	0.00052	0.54131
0.3	0.53365	0.09382	0.00797	0.00064	0.63609
0.4	0.54440	0.10115	0.00853	0.00066	0.65476
0.5	0.50858	0.09896	0.00834	0.00063	0.61653
0.6	0.43902	0.08871	0.00750	0.00057	0.53581
0.7	0.34558	0.07188	0.00614	0.00048	0.42409
0.8	0.23638	0.05017	0.00434	0.00034	0.29125
0.9	0.11878	0.02551	0.00224	0.00017	0.14672
1.0	0.00000	0.00000	0.00000	0.00000	0.00000
$\text{CHCl}_3(1)-\text{C}_6\text{H}_6(2)$					
0.0	0.00000	0.00000	0.00000	0.00000	0.00000
0.1	0.00216	-0.00430	-0.00037	-0.00002	-0.00254
0.2	-0.00085	-0.00899	-0.00078	-0.00006	-0.01069
0.3	-0.00707	-0.01349	-0.00118	-0.00009	-0.02185
0.4	-0.01474	-0.01730	-0.00153	-0.00012	-0.03370
0.5	-0.02220	-0.01994	-0.00178	-0.00014	-0.04408
0.6	-0.02782	-0.02095	-0.00186	-0.00014	-0.05079
0.7	-0.03007	-0.01991	-0.00179	-0.00015	-0.05194
0.8	-0.02730	-0.01637	-0.00148	-0.00011	-0.04528
0.9	-0.01787	-0.00988	-0.00089	-0.00007	-0.02872
1.0	0.00000	0.00000	0.00000	0.00000	0.00000
$\text{CHCl}_3(1)-\text{CCl}_4(2)$					
0.0	0.00000	0.00000	0.00000	0.00000	0.00000
0.1	-0.10410	-0.02118	-0.00156	-0.00010	-0.12697
0.2	-0.23786	-0.04959	-0.00347	-0.00022	-0.29116
0.3	-0.37799	-0.07820	-0.00525	-0.00031	-0.46177
0.4	-0.50939	-0.10249	-0.00674	-0.00040	-0.61903
0.5	-0.61897	-0.11930	-0.00780	-0.00045	-0.74653
0.6	-0.69230	-0.12636	-0.00839	-0.00050	-0.87757

0.7	-0.71031	-0.12150	-0.00837	-0.00054	-0.84073
0.8	-0.64380	-0.10230	-0.00737	-0.00050	-0.75371
0.9	-0.44195	-0.05395	-0.00488	-0.00035	-0.51115
1.0	0.00000	0.00000	0.00000	0.00000	0.00000
CCl₄(1)-CS₂(2)					
0.0	0.00000	0.00000	0.00000	0.00000	0.00000
0.1	0.98419	0.13492	0.01037	0.00080	1.13030
0.2	1.16619	0.19845	0.01372	0.00091	1.37928
0.3	1.14143	0.22584	0.01414	0.00083	1.38226
0.4	1.02399	0.22757	0.01324	0.00069	1.26551
0.5	0.85751	0.20876	0.01185	0.00059	1.07873
0.6	0.66506	0.17341	0.01018	0.00053	0.84920
0.7	0.46273	0.12623	0.00805	0.00046	0.59749
0.8	0.26591	0.07385	0.00528	0.00035	0.34540
0.9	0.09600	0.02607	0.00206	0.00015	0.12429
1.0	0.00000	0.00000	0.00000	0.00000	0.00000

Table IV. Activity Coefficients of Components 1 and 2 in Liquid-Vapor Interface.

x_1	$f_1(1)$	$f_2(1)$	$f_1(2)$	$f_2(2)$	$f_1(3)$	$f_2(3)$
C₆H₁₂(1)-C₆H₆(2)						
0.0	...	1.00000	...	1.00000	...	1.00000
0.1	2.86650	0.83570	1.36869	0.96792	1.21571	0.99416
0.2	2.29770	0.74375	1.28287	0.94823	1.17041	0.99313
0.3	1.93565	0.68509	1.21448	0.93806	1.13112	0.99696
0.4	1.68250	0.64548	1.15902	0.93599	1.09730	1.06593
0.5	1.49460	0.61852	1.11367	0.94145	1.06855	1.02056
0.6	1.34932	0.60099	1.07671	0.95455	1.04467	1.04170
0.7	1.23374	0.59136	1.04709	0.97616	1.02557	1.07065
0.8	1.14001	0.58908	1.02429	1.00788	1.01144	1.10942
0.9	1.06315	0.59458	1.00838	1.05263	1.00265	1.16111
1.0	1.00000	...	1.00000	...	1.00000	...
CCl₄(1)-C₆H₆(2)						
0.0	...	1.00000	...	1.00000	...	1.00000
0.1	1.79410	0.93012	1.25603	0.98255	1.15112	0.99683
0.2	1.61225	0.87962	1.20481	0.97002	1.12103	0.99670
0.3	1.47107	0.84265	1.16068	0.96294	1.09442	0.99978
0.4	1.35850	0.81583	1.12280	0.96033	1.07113	1.00631
0.5	1.26697	0.79713	1.09048	0.96245	1.05110	1.01657
0.6	1.19149	0.78536	1.06321	0.96948	1.03425	1.03299
0.7	1.12891	0.78008	1.04059	0.98176	1.02059	1.05016
0.8	1.07697	0.78120	1.02250	0.99994	1.01021	1.07488
0.9	1.03427	0.78912	1.00892	1.02492	1.00326	1.10617
1.0	1.00000	...	1.00000	...	1.00000	...
CHCl₃(1)-C₆H₆(2)						
0.0	...	1.00000	...	1.00000	...	1.00000

0.1	1.04303	0.99835	0.97199	1.00707	1.01069	1.00270
0.2	1.03034	0.99860	0.96955	1.01555	1.00468	1.00656
0.3	1.01993	1.00062	0.96864	1.02515	1.00006	1.01143
0.4	1.01173	1.00437	0.96915	1.03616	0.99673	1.01732
0.5	1.00551	1.00983	0.97100	1.04845	0.99459	1.02421
0.6	1.00103	1.01688	0.97420	1.06210	0.99358	1.03205
0.7	0.99827	1.02662	0.97868	1.07715	0.99364	1.04090
0.8	0.99719	1.03601	0.98447	1.09366	1.00476	1.05072
0.9	0.99779	1.04820	0.99158	1.11167	0.99689	1.06153
1.0	1.00000	...	1.00000	...	1.00000	...
CHCl ₃ (1)-CCl ₄ (2)						
0.0	...	1.00000	...	1.00000	...	1.00000
0.1	0.92195	1.03329	1.09988	1.01084	1.22057	1.00599
0.2	0.86122	1.08382	1.02786	1.03170	1.14032	1.01986
0.3	0.82594	1.14960	0.98071	1.06097	1.08507	1.04003
0.4	0.80756	1.23190	0.95040	1.09823	1.04652	1.06576
0.5	0.80218	1.33425	0.93273	1.14397	1.02002	1.09671
0.6	0.80836	1.46298	0.92548	1.19939	1.00267	1.13289
0.7	0.82640	1.62875	0.92784	1.26667	0.99282	1.17457
0.8	0.85892	1.85088	0.93989	1.34903	0.98939	1.22217
0.9	0.91188	2.16704	0.96294	1.45187	0.99183	1.27643
1.0	1.00000	...	1.00000	...	1.00000	...
CCl ₄ (1)-CS ₂ (2)						
0.0	...	1.00000	...	1.00000	...	1.00000
0.1	3.72468	0.78180	1.91645	0.92757	1.58273	0.97871
0.2	2.63858	0.71306	1.66706	0.89374	1.45521	0.97018
0.3	2.08657	0.68398	1.49142	0.88096	1.34971	0.97293
0.4	1.74400	0.67615	1.35903	0.88454	1.26160	0.98756
0.5	1.50836	0.68459	1.25558	0.90372	1.18810	1.01591
0.6	1.33660	0.70954	1.17316	0.94045	1.12730	1.06153
0.7	1.20725	0.75510	1.10740	1.00001	1.07799	1.13087
0.8	1.10930	0.83182	1.05612	1.09376	1.03965	1.23611
0.9	1.03839	0.96641	1.01921	1.24786	1.01272	1.40394
1.0	1.00000	...	1.00000	...	1.00000	...

IV. Discussions.

In this work all the values of E_{si} , a_i , θ_{si} , θ_{ii} , V_{si} and π_i for pure component i , which are listed in the table V, are assumed to be unperturbed in the solution.

They may be perturbed if the molecular shapes of the two components of the solution are different each other or if some chemical reactions occur between the component molecules due to the polarity, if any. In the regular

solutions, however, the perturbation is negligibly small, which, is reflected well in the result of this work. The calculated and the observed values for the vapor pressures, the partial pressures and the molar volumes of the liquid solutions are in good agreements as shown in the figure 1 and figure 2. The theoretical calculation of the partial molar volume is a success of this work, which is not found in

Table V. The Parametric Values for Pure Liquids.

	$C_6H_6^{21}$	$C_6H_{12}^{13}$	CCl_4^{21}	$CHCl_3^{11}$	CS_2^{11}
E_s (cal/mole)	10350	8823.2	8743.3	10036	9401.5
a (cal/mole)	468.2	281.2	179.0	504.1	646.7
θ_s (°K)	56.52	76.27	57.30	38.20	58.94
θ_s (°K)	49.04	75.15	54.54	31.00	40.58
V_s (cc/mole)	77.0	100.2	87.9	67.0	49.0
n	10.59	11.30	11.48	11.07	11.23

the earlier papers¹⁹⁻²¹.

As shown in the figure 3, the calculated surface tensions are higher than the observed ones by about 30 to 40%. The deviation are considered as due to the insufficient consideration of molecular orientation in the surface and the uncertainty of the molecular layer thickness, at least, in the top surface layer. However, the variations of the surface tensions with the mole fractions are in agreements with those of the observed.

In general, the component of lower surface tension is preferentially adsorbed at the liquid-vapor interface as shown in the figure 4. It can also be found that the variation with the mole fraction is in agreement between the calculated and the observed values of the adsorbed amounts.

As in the case of pure liquid, the most of the surface excess quantity results from the first top surface layer, and the contributions of the fourth layer and the belows are negligibly small between the temperatures of the normal melting point and the normal boiling point.

The calculated activity coefficients for the two components of liquid-vapor interface of the solution, shown in the table IV, may be useful for the further development of the liquid-vapor interface.

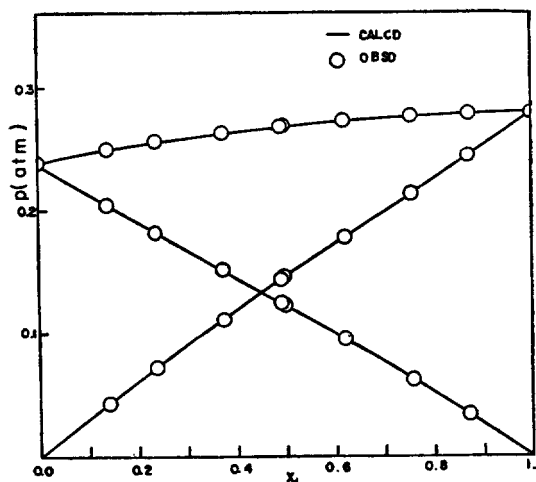


Fig. 1. Comparison of the calculated and the observed values²⁴ of the vapor pressure and the partial pressures for $CCl_4(1)-C_6H_6(2)$ at 313.15 °K.

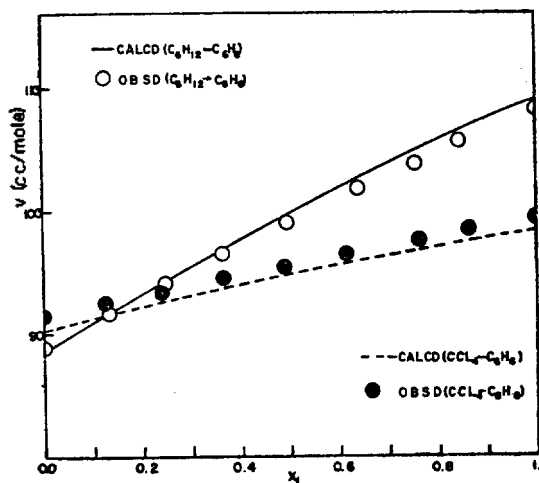


Fig. 2. Comparison of the calculated and the observed values^{23,24} of the molar volumes for $C_6H_{12}(1)-C_6H_6(2)$ at 293.15°K and $CCl_4(1)-C_6H_6(2)$ at 313.15°K.

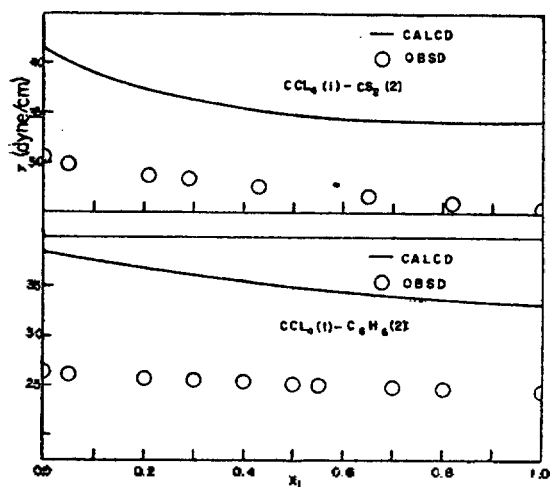


Fig. 3. Comparison of the calculated and the observed values²⁷ of the surface tensions for CCl₄(1)-CS₂(2) at 305.05°K and CCl₄(1)-C₆H₆(2) at 313.15°K.

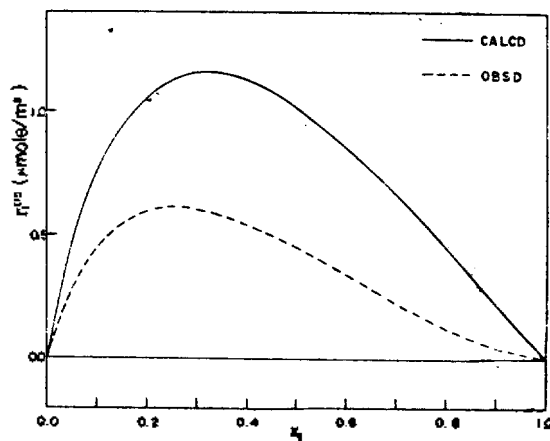


Fig. 4. Comparison of the calculated and the observed values²⁸ of the adsorbed amount at the liquid-vapor interface for C₆H₁₂(1)-C₆H₆(2) at 293.15°K.

V. Acknowledgment.

The author would like to express his sincere appreciation to professors Seihun Chang and Woon Sun Ahn for the discussions and the encouragements during this work.

VI. References.

1. E. A. Guggenheim, *Mixtures* (London: Oxford University Press, 1952).
2. A. Englert-Chwoles and I. Prigogine, *J. Chim. Phys.*, **55**, 16 (1958) and *Nouvo Cimento* (Suppl. 1), **9**, 347 (1958).
3. J. H. Hildebrand and R. L. Scott, *Solubility of Nonelectrolytes* (New York: Reinhold Pub. Corp., 1950), 3rd ed.
4. R. Defay and I. Prigogine, *Surface Tension and Adsorption* (New York: John Wiley and Sons, Inc., 1966).
5. J. J. Kipling, *Adsorption from Solutions of Non-Electrolytes* (London-New York: Academic Press., 1965).
6. C. A. Eckert and J. M. Prausnitz, *A.I.Ch.E. (Am. Inst. Chem. Engrs.) J.*, **10**, 677 (1964).
7. R. Defay and I. Prigogine, *Trans. Faraday Soc.*, **46**, 199 (1950).
8. A. Schuchovitzky, *Acta. Physicochim.*, **19**, 176 (1944).
9. S. W. Kim, M. S. Jhon, T. Ree and H. Eyring, *Proc. Natl. Acad. Sci.*, **59**, 336 (1968).
10. H. Eyring, T. Ree and N. Hirai, *ibid*, **44**, 683 (1958).
11. H. Pak, W. Ahn and S. Chang, *Daehan Hwahak Hwoejee (J. Korean Chem. Soc.)*, **10**, 18 (1966).
12. H. Pak and S. Chang, *ibid*, **10**, 91 (1966).
13. H. Lee and S. Chang, *ibid*, **10**, 129 (1966).
14. S. Kim, H. Pak, K. Kim and S. Chang, *ibid*, **11**, 105 (1967).
15. H. Pak, *ibid*, **12**, 18 (1968).
16. H. Lee, H. Pak and S. Chang, *ibid*, **12**, 32 (1968).
17. W. Ahn, H. Pak, J. Ryu, K. Kim and S. Chang, *ibid*, **12**, 190 (1968).
18. W. Ahn and S. Chang, *ibid*, **14**, 121 (1970).
19. W. Ahn, *ibid*, **10**, 136 (1966).

20. D. Choi, W. Ahn, K. Kim and S. Chang, *ibid*, 11, 143 (1967).
21. J. Ryu, W. Ahn, K. Kim and S. Chang, *ibid*, 12, 26 (1968).
22. S. Chang and H. Pak, *ibid*, 14, 111 (1970).
23. S. Chang, T. Ree, H. Eyring and I. Matzner, Progress in International Research on Thermodynamic and Transport Properties (J. F. Masi and D. H. Tsai ed.), p 33, Princeton University Press. (Princeton, New Jersey, 1962).
24. G. Scatchard, S. E. Wood and J. M. Mochel, *J. Am. Chem. Soc.*, 62, 712 (1940).
25. S. E. Wood and A. E. Austin, *ibid* 67, 480(1945).
26. S. E. Wood and J. P. Brusie, *ibid*, 65, 1891 (1943).
27. M. M. Chaudhri, P. K. Katti and M. N. Baliga, *Trans. Faraday Soc.*, 55, 2013 (1959).
28. J. J. Kipling, Proceedings of the Third International Congress of Surface Activity (Mainz: Verlag der Universitätsdruckerei, 1960), vol 2, p 77.