

**Semiempirical Equation of State for the Infinite Dilution
Thermodynamic Functions of Hydration of Nonelectrolytes over
Wide Ranges of Temperature and Pressure**

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Abstract

The recently proposed model [4,5] for correlating the infinite dilution partial molar properties of aqueous nonelectrolytes is briefly outlined. The approach is fundamentally based on the $A_{12} = V_2^{\circ} / \kappa RT$ parameter, related to the infinite dilute solute – water direct correlation function integral. The A_{12} parameter is considered as a semiempirical function of temperature and density. At supercritical temperatures thermodynamic integrations of this function allow calculation of all thermodynamic functions of hydration (V_2° , $\Delta_h G^{\circ}$, $\Delta_h H^{\circ}$ and $\Delta_h Cp^{\circ}$) of a solute. An extension to subcritical conditions is done using an auxiliary $\Delta_h Cp^{\circ}(T, P_r)$ -function, which describes the temperature course of the heat capacity of hydration of a solute at $P=28$ MPa and subcritical temperatures. The variations of the $\Delta_h Cp^{\circ}(T, P_r)$ -function are constrained by known values of $\Delta_h G^{\circ}$, $\Delta_h H^{\circ}$ and $\Delta_h Cp^{\circ}$ at ambient and supercritical conditions. This model, which was used earlier to correlate properties of a few dissolved gases, is successfully employed here to describe V_2° , $\Delta_h G^{\circ}$, $\Delta_h H^{\circ}$ and $\Delta_h Cp^{\circ}$ experimental results for a number of aqueous nonelectrolytes, including ones of high polarity (alcohols, amines, acids, amides) and/or large size (hexane, benzene).

1. Introduction

Accurate estimates of thermodynamic properties of aqueous solutions at elevated temperatures and pressures are required for use in geochemistry, chemical technology and power energetics. Detailed experimental studies are feasible only for a limited number of compounds and for a majority of aqueous solutes the thermodynamic properties have to be predicted in the framework of correlating models. A number of such approaches exist [1-3 and others]. Recently, we proposed a new model to correlate the infinite dilution partial molar thermodynamic functions of hydration of nonelectrolytes over wide ranges of conditions, up to 1300 K and pressures corresponding to pure water densities up to 1000 kg·m³ [4,5]. The model was fine tuned using experimental high-temperature determinations of partial molar volumes and heat capacities of a few extensively studied nonelectrolytes [6-9]: CH₄, CO₂, H₂S, NH₃, C₂H₄, Ar, Xe. The goal of this work is to check the quality of the model's performance for some more complex nonelectrolytes, including polar ones and ones of a large size.

2. A brief outline of the new model

Following recommendations of O'Connell [10] we have chosen as a basic correlating parameter the function $A_{12} = V_2^0 / \kappa RT$, which is related to the water – infinite dilution solute direct correlation function integral, C_{12} , by means of $A_{12} = 1 - C_{12}$, where V_2^0 represents the partial molar volume of a solute, κ stands for isothermal compressibility of pure water, and R and T stand for the gas constant and temperature in Kelvin, respectively. This choice of the basic correlating parameter has an important advantage: the function A_{12} is smooth and finite everywhere, even at the critical point of a solvent. Its range of variation is much smaller, than, for example, that of V_2^0 , which strongly diverges at near-critical conditions.

The parameter A_{12} has qualitatively understandable density (ρ) and temperature dependencies [4,11]: equal to one at $\rho=0$ with a linear initial density dependence; positive and rapidly increasing at high densities; well-behaved in the solvent critical region. These features can easily be seen [4] for the function $A_{11} = V_1^0 / \kappa RT$, calculated from precise PVT-properties of water, where V_1^0 stands for the molar volume of water. The function A_{11} can be considered as an analog of A_{12} for the case of similarity of species 1 and 2 (the principal difference is the non-zero value for A_{12} at the critical point of water: if water-solute direct correlations are more positive than water-water direct correlations, then $A_{12}<0$, otherwise $A_{12}>0$). Finally, A_{12} and A_{11} can be expanded in a virial series [10]: $A_{ij} = 1 + 2\rho B_{ij} + \dots$, where B_{ij} is the second cross virial coefficient between species i and j .

Such considerations led to the equation for A_{12} as a function of temperature and density [4]:

$$A_{12} = NA_{11} + (1 - N) + 2\rho\{B_{12} - NB_{11}\}\exp[-c_1\rho] + \rho\left(a/T^5 + b\right)\left(\exp[c_2\rho] - 1\right), \quad (1)$$

where N , a , b are the fitting parameters; B_{11} and B_{12} stand for the second virial coefficient of water and the second cross virial coefficient; $c_1=0.0033 \text{ m}^3\cdot\text{kg}^{-1}$ and $c_2=0.002 \text{ m}^3\cdot\text{kg}^{-1}$ are universal constants. At the limit of low densities Eq.(1) correctly transforms into a virial equation truncated at the second virial coefficient. The physical meaning of the fitting parameters can be qualitatively understood as follows. Water serves as a reference solute. The parameter N reflects the difference in sizes between a solute and water, b is expected to correct the difference in the shape between A_{11} and A_{12} functions, and the parameter a is needed mainly to compensate for an unrealistically large contribution of the term containing $B_{12}-NB_{11}$ at high densities and low temperatures. The temperature dependencies of B_{11} and B_{12} are described by a simple analytical relation valid for the square-well

potential: $B_{ij} = 2\pi N_A \sigma_{ij}^3 / 3 \left\{ 1 - (\lambda^3 - 1) \left[\exp[\varepsilon_{ij} / k_B] - 1 \right] \right\}$, where N_A and k_B stand for Avogadro's number and Boltzmann's factor; σ_{ij} , ε_{ij}/k_B and $\lambda=1.22$ are the parameters of the square-well potential. For many solutes these parameters can be evaluated independently using experimental or estimated values of B_{12} .

Eq. (1) results in $V_2^\circ = \kappa R T A_{12}$. At temperatures exceeding the critical temperature of water Eq. (1) can be integrated [11] to give for the infinite dilution fugacity coefficient of a solute, Φ_2° : $\ln \Phi_2^\circ = \int_0^p (A_{12} - 1) / \rho dp - \ln P V_1^\circ / R T$. As a consequence, the infinite dilution partial molar thermodynamic caloric functions of hydration for a solute: the Gibbs energy, $\Delta_h G^\circ$, the enthalpy, $\Delta_h H^\circ$, the entropy $\Delta_h S^\circ$, and the heat capacity, $\Delta_h C_p^\circ$, are calculated by means of: $\Delta_h G^\circ = R T \left\{ \ln(\Phi_2^\circ P / P^\circ) - \ln(1000 / M_w) \right\}$; $\Delta_h H^\circ = -T^2 \left(\partial(\Delta_h G^\circ / T) / \partial T \right)_p$; $\Delta_h S^\circ = -\left(\partial \Delta_h G^\circ / \partial T \right)_p$; and $\Delta_h C_p^\circ = \left(\partial(\Delta_h H^\circ) / \partial T \right)_p$. Here $P^\circ = 0.1$ MPa stands for the ideal gas reference pressure, M_w is the molar mass of water in $\text{g}\cdot\text{mol}^{-1}$. The equations for $\Delta_h G^\circ$ and $\Delta_h S^\circ$ are valid when the standard state adopted for aqueous species is unit activity in a hypothetical one molal solution referenced to infinite dilution. The complete analytical statements consistent with Eq. (1) are given in [4,5].

However, these equations do not give the quantitatively correct results at temperatures below the critical temperature of pure water, where the two-phase region exists for the solvent. To overcome this problem and extend the model into subcritical temperatures, we introduced [5] an auxiliary function, $\Delta_h C_p^\circ(T, P_r)$, which describes the temperature dependence of the infinite dilution partial molar heat capacity of a solute at pressure $P_r=28$

MPa and temperatures below some “switching” temperature T_s . Above the “switching” temperature all the caloric functions of hydration are calculated by means of integrated forms of Eq. (1), below T_s the $\Delta_h Cp^0(T, P_r)$ -function and its integrated form are used for these purposes.

How the $\Delta_h Cp^0(T, P_r)$ -function is defined? As a rule, there are experimental determinations of $\Delta_h G^0$, $\Delta_h H^0$ and $\Delta_h Cp^0$ at 298.15 K and 0.1 MPa, which can be recalculated to $P_r=28$ MPa. Combining this information with estimates of $\Delta_h G^0$, $\Delta_h H^0$ and $\Delta_h Cp^0$ at some supercritical temperature T_s one obtains four constraints to the variations of the $\Delta_h Cp^0(T, P_r)$ -function: the numerical values of the temperature increments between 298.15 K and T_s for the Gibbs energy and the enthalpy of hydration, and the numerical values of the heat capacity of hydration at 298.15 K and T_s , all at $P_r=28$ MPa. These four constraints were used [5] to determine the optimal analytical form of the four-term $\Delta_h Cp^0(T, P_r)$ -function by globally fitting all available (V_2^0 , $\Delta_h G^0$, $\Delta_h H^0$ and $\Delta_h Cp^0$) data for the well-studied solutes CH_4 , CO_2 , H_2S , NH_3 , C_2H_4 , Ar, Xe:

$$\Delta_h Cp^0(T, P_r) = d_0 + d_1 T + d_2 T \exp(T/\Theta) - d_3 n(n-1)(T_0 - T)^{n-2}, \quad (2)$$

where $d_{0,3}$ are the Eq.(2) parameters, $n=0.6$ and $\theta=40$ K are universal constants, $T_0=669$ K, the approximate temperature of extrema for the temperature and pressure derivatives of the molar volume of water at $P_r=28$ MPa. As there are four constraints to determine the four parameters of Eq. (2), then the application of this method does not require new additional fitting parameters besides the experimental values of the thermodynamic functions of hydration at 298.15 K. Experience has shown that using $T_s=658$ K, slightly higher than T_c , gives the best results. Once the $\Delta_h Cp^0(T, P_r)$ -function is determined, values of $\Delta_h G^0$,

$\Delta_{\text{h}}H^{\circ}$ and $\Delta_{\text{h}}Cp^{\circ}$ can be recalculated to other pressures using the thermodynamic relations

$$\Delta_{\text{h}}G^{\circ}(T, P) - \Delta_{\text{h}}G^{\circ}(T, P_r) = \int_{P_r}^P V_2^{\circ} dP; \Delta_{\text{h}}H^{\circ}(T, P) - \Delta_{\text{h}}H^{\circ}(T, P_r) = \int_{P_r}^P (V_2^{\circ} - T(\partial V_2^{\circ} / \partial T)) dP;$$

$$\Delta_{\text{h}}Cp^{\circ}(T, P) - \Delta_{\text{h}}Cp^{\circ}(T, P_r) = -T \int_{P_r}^P (\partial^2 V_2^{\circ} / \partial T^2) dP, \text{ see [4,5].}$$

The method described above allows the reproduction of experimental values of V_2° , $\Delta_{\text{h}}G^{\circ}$, $\Delta_{\text{h}}H^{\circ}$ and $\Delta_{\text{h}}Cp^{\circ}$ for CH_4 , CO_2 , H_2S , NH_3 , C_2H_4 , Ar, Xe with an accuracy close to the experimental uncertainties [4,5].

3. Test of the model

Our goal of proposing an accurate model for correlating thermodynamic properties of aqueous nonelectrolytes with a small number of fitting parameters (N, a, b) was achieved through a fairly stiff construction, where the temperature course of the subcritical heat capacities for a solute is calculated using the values of $\Delta_{\text{h}}G^{\circ}$, $\Delta_{\text{h}}H^{\circ}$ and $\Delta_{\text{h}}Cp^{\circ}$ generated by the model. Can this approach be used for a wide variety of nonelectrolytes including ones of high polarity and/or large size? To answer this question we performed a global fit for a number of compounds for which experimental data (V_2° , $\Delta_{\text{h}}G^{\circ}$, $\Delta_{\text{h}}H^{\circ}$ and $\Delta_{\text{h}}Cp^{\circ}$) are available up to at least 500 K. For most of these solutes experimental values of B_{12} are absent. Given this situation we decided to determine the values of ε_{12}/k_B by a global fit of the data, increasing the total number of fitting parameters to four (N, a, b, ε_{12}/k_B). Values of σ_{12} (10^{-10} m) were found using empirical correlations with the partial volume of at 298 K, $V_2^{\circ}(298)$, or the critical volume of a compound, V_c , in $\text{cm}^3 \cdot \text{mol}^{-1}$: $\sigma_{12} = 0.87 \cdot V_2^{\circ}(298)^{1/3}$ and $\sigma_{12} = 0.97 + 0.44 \cdot V_c^{1/3}$. These correlations are based on the values of σ_{12} for solutes

for which experimental determinations of B_{12} are available, see [4]. Results of the overall fit are given in Table 1. The values of the fitting parameters are given together with their uncertainties at the 0.95 confidence level (shown in parentheses as the confidence interval of the last digits, i.e. 6.43(42) means 6.43 ± 0.42 and 17.0(38) means 17.0 ± 3.8). The format of this paper does not allow citing all the sources of experimental data employed, however, the major references to the results at $T > 373$ K are [12-32].

The first test of the reliability of this procedure is to compare B_{12} calculated using ϵ_{12}/k_B from the global fit with the experimental values of the second cross virial coefficients. Values of B_{12} for cyclohexane and methanol from experiments (symbols), predictions from the Hayden-O'Connell [33] correlation (dashed line), and calculations using σ_{12} and ϵ_{12}/k_B from Table 1 are plotted in Fig.1. Experimental results are taken for cyclohexane from [34] and for methanol from [35]. The Hayden-O'Connell correlation closely predicts values of B_{12} (note that both sets of data were measured after the correlation was published). In general, the fitting procedure gives reasonable estimates of B_{12} at temperatures above 450 K. At lower temperatures there is a systematic deviation from the measured data, which is most prominent for methanol. These results are expected, because the relation based on the square-well potential, especially with a fixed value of λ , can not accurately describe B_{12} data over very wide temperature ranges. The low-temperature deviations of experimental and calculated B_{12} values are not crucial for the performance of the present approach, because the contribution of the term containing B_{12} - NB_{11} at low temperatures and high densities is compensated by the parameter a , see above. From a practical point of view, determination of the ϵ_{12}/k_B parameter by an overall fit for well-studied solutes seems justified. In addition, these results suggest that for many solutes,

including those that are large and/or polar, parameters σ_{12} and ϵ_{12}/k_B can be estimated independently using B_{12} values generated by the Hayden-O'Connell correlation over the temperature range 450-1000 K.

Another test is the quality of the description of the experimental data. Some results are presented graphically in Fig. 2-5. In general, the model provides a close reproduction of all the variety of data for both nonpolar (hydrocarbons) and strongly polar (carboxylic acids) compounds, including compounds of large size. In cases, where deviations are prominent (V_2° for cyclohexane at low temperatures, $\Delta_h G^\circ$ at $T > 523$ K), experimental results may bear considerable uncertainties. An objective characteristic of the quality of the fit is the

standard weighted deviation,
$$\text{SWD} = \left[\sum_i \left(\frac{\Delta_i}{\delta_i} \right)^2 / (N_p - m) \right]^{1/2}$$
, where Δ stands for the

difference between experimental and calculated data, δ is the uncertainty of the experimental point, N_p and m stand for the total number of data points and the number of adjustable parameters, respectively. Values of SWD are given in the last column of Table 1 for the present model, the Sedlbauer-O'Connell-Wood model, SOCW [3], and the revised HKF-model [1,2], respectively. Despite the lower number of adjustable parameter (four compared to five for the SOCW and seven for the HKF-models), the present approach is very competitive in the quality of data description. In general, we note that the present model and the SOCW model, both fundamentally based on the A_{12} parameter, perform for aqueous nonelectrolytes considerably better than the Born-type revised HKF-model.

Conclusion

The recently proposed [4,5] model for correlating the infinite dilution partial molar properties of aqueous nonelectrolytes is briefly outlined. The model, earlier used to

correlate properties of a few dissolved gases, is successfully employed to describe the V_2^0 , $\Delta_h G^0$, $\Delta_h H^0$ and $\Delta_h C_p^0$ experimental results for a number of aqueous nonelectrolytes, including ones of high polarity (alcohols, amines, acids, amides) and/or large size (benzene, hexane). The success of this model with these solutes and the use of only four fitting parameters leads us to postulate that the model will provide reasonable estimates of thermodynamic properties outside the range of experimental measurements.

List of symbols

A_{12}	Correlating function, $A_{12} = V_2^0 / \kappa RT$
a	Model parameter
B_{ij}	Second virial coefficient
b	Model parameter
C_{ij}	Direct correlation function integral
C_p	Heat capacity
d_{0-3}	Parameters of Eq.(2)
G	Gibbs energy
H	Enthalpy
k_B	Boltzmann's factor
m	Number of adjustable parameters
N	Model parameter
N_A	Avogadro's number
N_p	Number of experimental point
n	Universal constant of Eq. (2), $n=0.6$

P	Pressure
R	Gas constant
T	Temperature
T_c	Critical temperature of water
T_o	Universal constant of Eq. (2), $T_o=669$ K
V	Volume

Greek letters

Δ	Change in thermodynamic function; the difference between an experimental and fitted data point
ϵ_{ij}	Parameter of the square-well potential
κ	Isothermal compressibility of water
λ_{ij}	Parameter of the square-well potential
θ	Universal constant of Eq. (2), $\theta=40$ K
ρ	Density of water
σ_{ij}	Parameter of the square-well potential

Superscripts

^o	Infinite dilution
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Subscripts

c	Critical
h	Hydration

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FIGURE CAPTIONS

- Fig.1. Values of the second cross virial coefficients as the function of temperature: experimental results (symbols, from [34,35]), the Hayden-O'Connell correlation's predictions (dashed lines), calculated using ϵ_{12}/k_B values from the global fit (solid lines).
- Fig.2. Experimental (symbols, from [23,26,27,31]) and fitted (solid lines) values of V_2° for a number of aqueous nonelectrolytes.
- Fig.3. Experimental (symbols, from [20,21,24,28 and other sources]) and fitted (lines) values of $\Delta_h C_p^\circ$ for some nonelectrolytes. Open circles and solid lines refer to the saturated water vapor pressure, filled triangles and dashed lines refer to the pressure of 28 MPa.
- Fig.4. Experimental (symbols, from [27]) and fitted (lines) values of $\Delta_h H^\circ$ for n-hexane and benzene.
- Fig.5. Experimental (symbols, from [12-16,32 and other sources]) and fitted (lines) values of $\Delta_h G^\circ$ for a number of nonelectrolytes.

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Table 1. Results of the global fit for large and/or polar aqueous nonelectrolytes, see text.

Nonelectrolyte	N of points ^a	$\Delta_h G^{\circ b}, \Delta_h H^{\circ b}, \Delta_h C_p^{\circ c}$	$\sigma_{12}^d, \epsilon_{12}/k_B^e$	N, $a \cdot 10^{-9}{}^f, b \cdot 10^3{}^g$	SWD ^h
Hexane	18, 2, 14, 26	18.12, -31.6, 518	4.18, 585(43)	6.43(42), -15.1(38), 3.11(26)	1.18, 1.84, 5.06
Cyclohexane	19, 2, 16, 26	12.95, -33.1, 410	3.90, 585(43)	5.60(48), -17.0(38), 2.63(26)	1.53, 1.61, 4.94
Benzene	39, 22, 36, 73	4.29, -31.7, 290	3.78, 710(13)	4.26(9), -8.22(58), 2.00(9)	0.97, 2.42, 6.67
Toluene	28, 8, 19, 26	4.55, -36.3, 359	3.99, 656(24)	5.28(27), -11.1(18), 2.14(7)	1.54, 2.83, 5.21
n-Propylamine	8, 4, 3, 3	-10.40, -56.0, 241	3.66, 845(49)	3.60(31), -5.6(12), 1.90(59)	1.13, 0.79, 2.53
1-Propanol	33, 26, 17, 29	-12.38, -57.65, 268	3.61, 929(24)	3.20(13), -3.86(34), 2.10(32)	0.80, 0.85, 1.61
Ethanol	39, 22, 36, 73	-13.00, -52.59, 199	3.35, 975(54)	2.53(25), -2.68(63), 1.44(62)	0.73, 0.71, 0.87
Methanol	72, 22, 28, 51	-13.21, -45.13, 114	3.03, 927(20)	1.88(8), -1.87(29), 0.64(15)	0.90, 0.79, 1.01
Propionic acid	14, 13, 0, 15	-20.35, -56.5, 165	3.59, 1046(17)	3.47(13), -4.85(40), 1.56(27)	0.83, 1.21, 1.75
Acetic acid	23, 41, 15, 60	-21.00, -52.8, 105	3.32, 1087(8)	2.84(4), -3.88(16), 0.84(6)	0.73, 1.07, 1.55
Propionamide	11, 13, 0, 0	-31.5, -73.4, 168	3.71, 1064(18)	3.82(14), -4.53(50), 1.02(31)	0.84, 1.02, 1.91

^a Number of $V_2^{\circ}, \Delta_h C_p^{\circ}, \Delta_h H^{\circ}, \Delta_h G^{\circ}$ points, respectively; ^b $\text{kJ} \cdot \text{mol}^{-1}$, at 298.15 K, 0.1 MPa; ^c $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, at 298.15 K, 0.1 MPa; ^d 10^{-10} m ; ^e K; ^f $\text{m}^3 \cdot \text{K}^5 \cdot \text{kg}^{-1}$; ^g $\text{m}^3 \cdot \text{kg}^{-1}$; ^h the standard weighted deviation, SWD, is given for this model, the SOCW model [3], and the revised HKF-model [1,2], respectively.

Fig.1

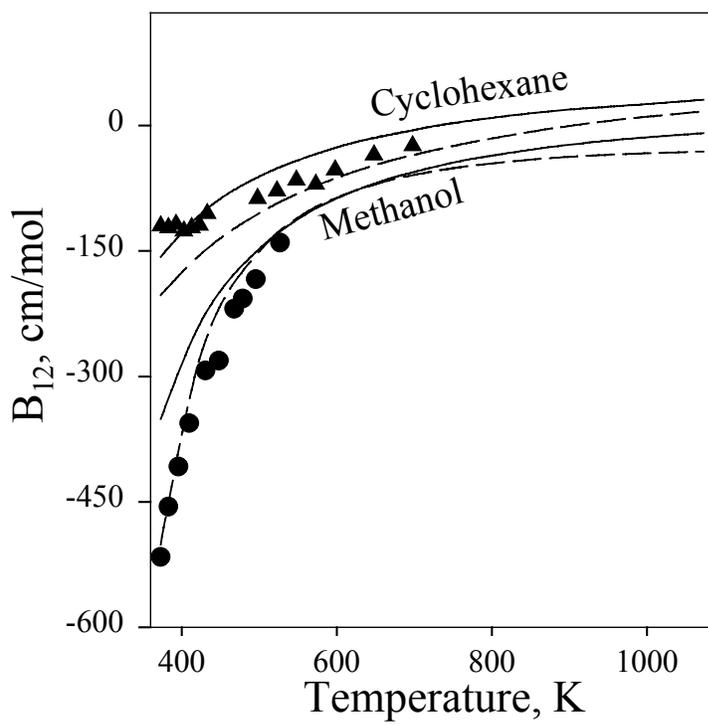


Fig.2

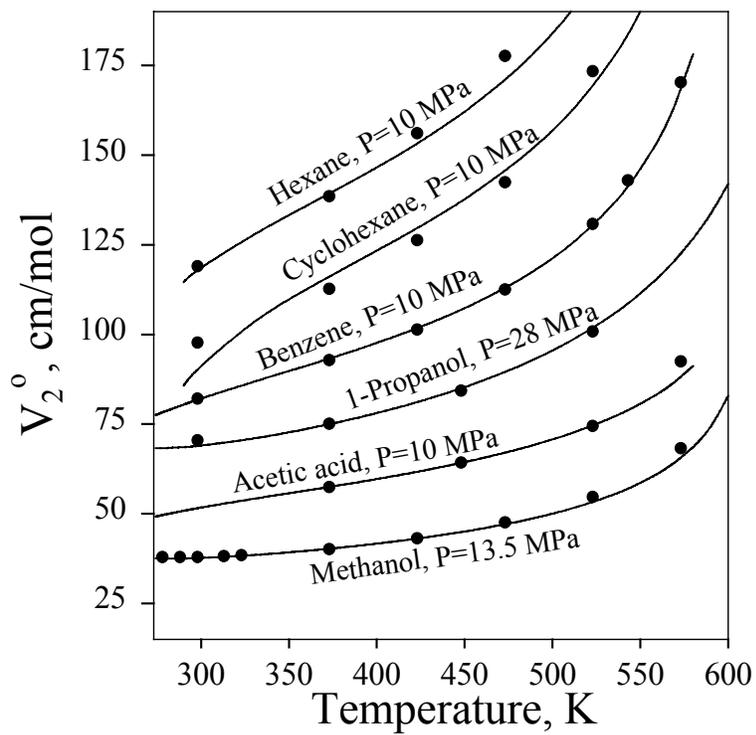


Fig.3

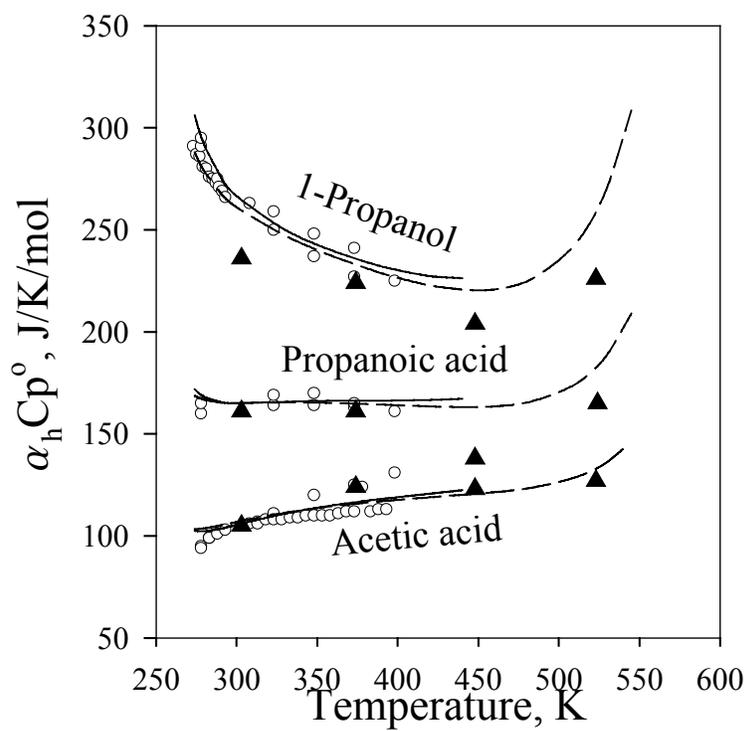


Fig.4

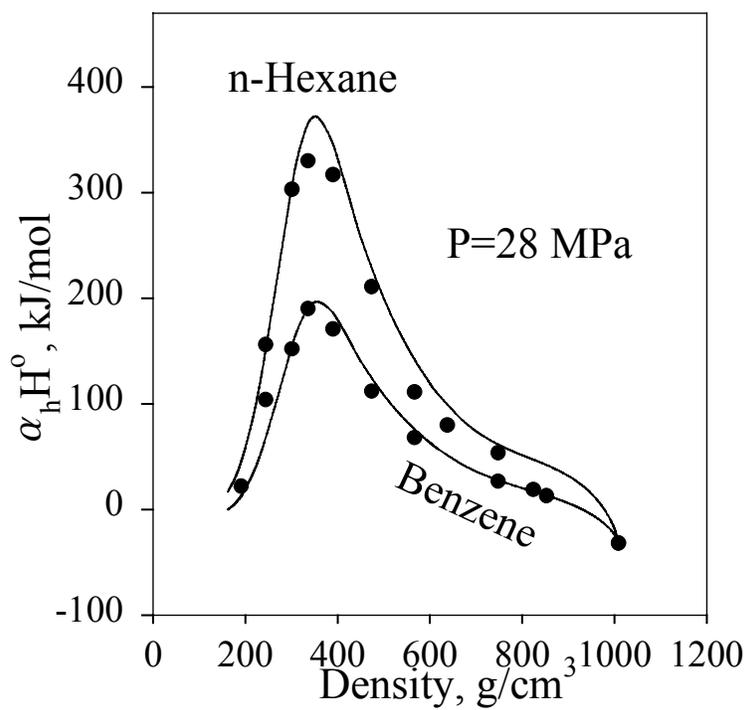


Fig.5

