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Equation of State for C_{60} Fullerene Aqueous Solutions

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In the present work PVT data of the C_{60} fullerene aqueous solution (C_{60}FAS) were measured as a function of the concentration of C_{60} molecules using the variable cell method with metal bellows in the temperature range from 295 to 360 K at pressures from 0.1 to 103.2 MPa. On the liquid–vapor equilibrium line the density (ρ) of the C_{60}FAS was measured using the pycnometer method. As a result, numerical values for the isothermal modulus of elasticity (K_T), isobaric expansivity (α_P), isothermal deviation of entropy factor ($T\Delta S$), enthalpy (ΔH), and internal energy (ΔU) have been determined. Finally, an equation of state for the C_{60}FAS was obtained for the first time.

KEY WORDS: equation of state; fullerene aqueous solution; high pressures.

1. INTRODUCTION

Fullerenes are currently being widely investigated and have potential for various technical applications [1]. In particular, for biomedical testing, water-soluble forms of fullerenes are of great interest. It is known that fullerenes are an allotropic form of carbon that consists of polyhedral sphere-like molecules with the number of carbon atoms from 60 to 240.

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The exotic structure of fullerenes makes for their unusual behavior in solutions [2–8]. In particular, the C_{60}fullerene aqueous solution (C_{60}FAS) is shown to be an ultra-microheterogeneous and polydisperse system containing spherical C_{60} aggregates (both single fullerene C_{60} molecules and their fractal clusters, with diameters from 7 to 36 nm) in a hydrated state (i.e., the fullerene aggregates are covered by a strong hydrated shell) [4, 5]. The indirect optical transitions revealed also unequivocally prove the existence of the crystalline state of fullerene molecules as C_{60} fullerene aggregates in the water [8]. Hence, more detailed experimental and theoretical studies of the structure and thermophysical properties of the C_{60}FAS are important.

In this paper we present the results of studies of the thermodynamic properties of the C_{60}FAS with C_{60} concentrations of $X_1 = 0.05\ \mathrm{mg\cdot ml^{-1}}$, $X_2 = 0.10\ \mathrm{mg\cdot ml^{-1}}$, $X_3 = 0.18\ \mathrm{mg\cdot ml^{-1}}$, and $X_4 = 0.28\ \mathrm{mg\cdot ml^{-1}}$.

2. MEASUREMENTS

PVT measurements for the C_{60}FAS were carried out in the range of pressures from 0.1 to 103.2 MPa at temperatures from 295 to 360 K with variable cell method with a metal bellows and differential inductive sensor of linear shifts [6–9]. The uncertainty in the pressure measurement was 0.05% of the actual measured value. The density and temperature measurement uncertainties were less than 0.1%. The density of pure water was found in the review [10].

3. RESULTS

The thermobaric dependence of the density ρ ($\mathrm{kg\cdot m^{-3}}$) of investigated solutions is given in Table I and Fig. 1. As one can see, the addition of fullerene C_{60} into water results in a shallow density growth at normal pressure. But when the pressure increases, the density curves for the investigated solutions reveal less steepness as compared to pure water. Higher concentrations of C_{60}FAS correspond to less steepness of density curves. This fact results in a decrease of compressibility of the C_{60}FAS with an increase of C_{60}concentration.

Thermodynamic properties such as the isothermal elastic modulus K_T, isobaric expansivity α_P, entropy factor $T\Delta S$, enthalpy ΔH, and total internal energy ΔU were calculated according to the general thermodynamic formulas [11]

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P,$$

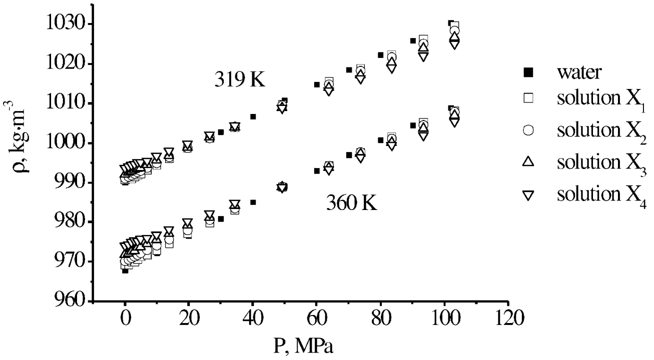

Fig. 1. Themobaric dependence of density ρ (kg·m^{-3}) at 319 and 360 K.

Table I. Thermobaric Dependence of Density ρ (kg·m^{-3}) for the C_{60}FAS

		T (K)			
X (mg·ml^{-1})	P (MPa)	295	319	342	360
X_1=0.05	0.1	998	991	979	969
	7.0	1001	993	982	972
	49.2	1019	1010	999	989
	103.2	1039	1030	1018	1008
X_2=0.10	0.1	999	991	980	970
	7.0	1002	994	982	973
	49.2	1019	1010	998	989
	103.2	1038	1028	1017	1008
X_3=0.18	0.1	999	992	982	972
	7.0	1002	994	984	974
	49.2	1017	1009	998	989
	103.2	1037	1027	1016	1007
X_4=0.28	0.1	1001	994	984	974
	7.0	1003	996	985	976
	49.2	1017	1009	998	989
	103.2	1035	1025	1014	1005

$$K_T = -V\left(\frac{\partial P}{\partial V}\right)_T,$$

$$T\Delta S = -T\int_{P_0}^{P}\left(\frac{\partial V}{\partial T}\right)_P dP,$$

$$\Delta U = -T\int_{P_0}^{P}\left(\frac{\partial V}{\partial T}\right)_P dP, -\int_{V_0}^{V} P dV,$$

$$\Delta H = \int_{P_0}^{p}\left(V - T\left(\frac{\partial V}{\partial T}\right)_p\right) dP.$$

The obtained results for some isotherms are presented in Fig. 2–6. As shown in Figs. 2 and 3, the isobaric expansivity α_P in solutions decreases, and the isothermal elastic modulus K_T increases with an increase of C_{60} concentration. Consequently, one can assume that the energy of molecular interaction in the investigated solutions is an increasing function of concentration. The isothermal deviations of the entropy factor $T\Delta S$ (see Fig. 4) and the total internal energy ΔU (see Fig. 5) are of the same relative character. Deviations of these properties are higher for the solutions than for pure water. When the pressure increases, the absolute values of these isothermal deviations also increase. The isothermal deviation of enthalpy ΔH (see Fig. 6) is higher in solutions than in pure water. The increase of ΔH with the addition of C_{60} fullerene into water is not so great as for the entropy factor $T\Delta S$ and the total internal energy ΔU. Thus, we can conclude that the increase of internal energy is defined by its entropy term.

In order to describe analytically the pressure dependence of the thermodynamic properties for the C_{60}FAS, we used the following simple empirical isothermal equations of state with a few parameters employing statistical analysis [12]:

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{A'}{B+P} \text{ (Tait)}, \tag{1}$$

$$\ln\frac{PV^{2/3}}{V_0^{1/3} - V^{1/3}} = A_0 + B_0(V_0^{1/3} - V^{1/3}) \text{ (Hudleston)}, \tag{2}$$

$$\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{A^*}{B^* + P} \text{ (Murnaghan)}, \tag{3}$$

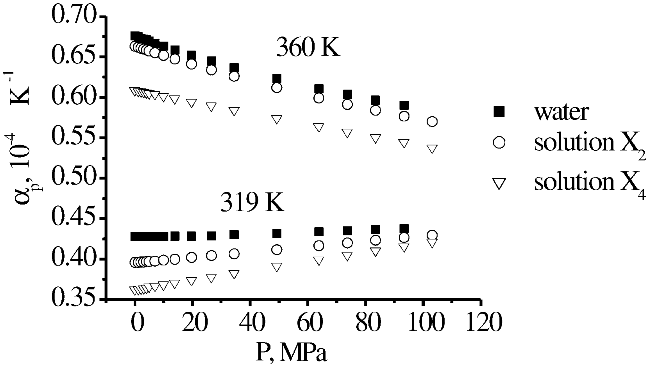

Fig. 2. Isobaric expansivity α_P at 319 and 360 K.

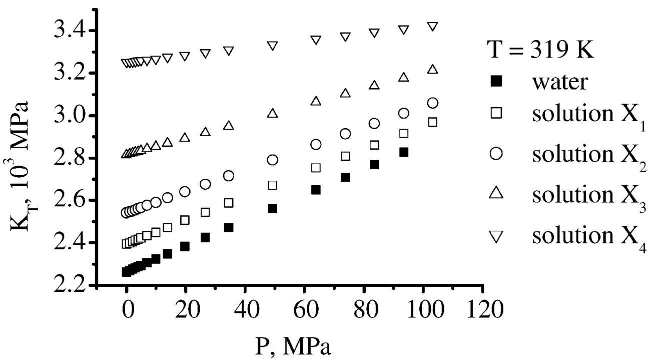

Fig. 3. Isothermal elastic modulus K_T at 319 and 360 K.

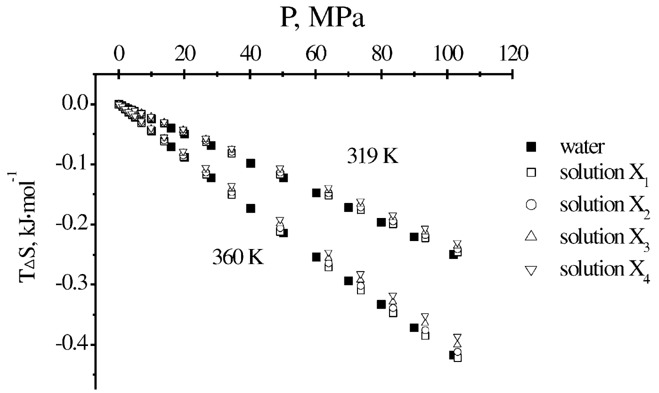

Fig. 4. Isothermal deviation of entropy factor $T\Delta S$ at 319 and 360 K.

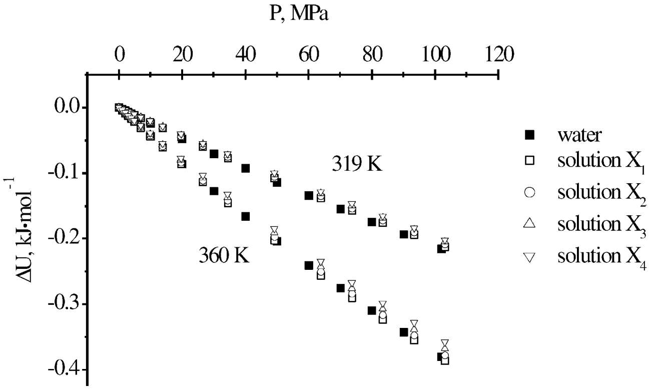

Fig. 5. Isothermal deviation of total internal energy ΔU at 319 and 360 K.

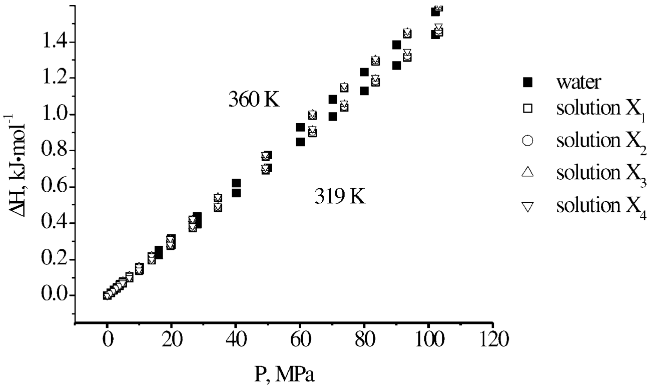

Fig. 6. Isothermal deviation of enthalpy ΔH at 319 and 360 K.

$$P = \frac{a}{V^2} + \frac{b}{V^9} \text{ (Ahoondov–Mamedov)}, \tag{4}$$

$$P = \frac{a^*}{V^3} + \frac{b^*}{V^7} \text{ (Goloobev–Gooseinov)}, \tag{5}$$

$$P = \frac{B'}{V - A'} + C' \text{ (Biron–Mamedov)}. \tag{6}$$

In order to decide which of these equations is preferred, all of them were rearranged to the form containing the same quantities defined in the experiment [12]; P_0 is the reference (normal) pressure, ρ_0 is the reference density, $K_{T,0}$ is the elastic modulus in the reference state, and $\left.\frac{\partial K_T}{\partial P}\right|_{T,0}$ is its derivative. Experimental values of $(P-P_0)/K_{T,0}$ were fitted according to the above mentioned equations of state. Qualitative comparisons among Eqs. (1) to (6) and experiment were tested using the χ^2-criterion [13] (see Table II). As one can see in Table II, all these equations are indistinguishable and describe experiment equally well up to pressures 50 MPa. They only deviate from experiment at higher pressures. A better fit of experimental $(P-P_0)/K_{T,0}$ vs. P dependence is given by Tait, Hudleston, and Murnaghan equations of state. In order to choose the most reliable of these three equations, we have plotted the isothermal derivative $\left(\frac{\partial P}{\partial V}\right)_T$ as a function of pressure (see Fig. 7). It was found to be linear with a random mean-square deviation (RMSD) of less than 0.8% for all C_{60}FAS investigated. As follows from the analytical forms of Eqs. (1)–(6), the only equation of state leading to the linear character of $\left(\frac{\partial P}{\partial V}\right)_T$ vs. P dependence is the Tait equation. Thus, it was accepted as the most reliable.

The integral form of the Tait equation (Eq. (1)) is as follows:

$$V = V_0\left(1 - A\ln\frac{B+P}{B+P_0}\right), \tag{7}$$

$$P = (B+P_0)\exp\frac{V_0-V}{AV_0} - B, \tag{8}$$

Table II. Some $(P-P_0)/K_{T,0}$ Values for the C_{60}FAS with Concentration X_4= 0.28 mg.ml^{-1} at 360 K

	$(P-P_0)/K_{T,0}$						
P(MPa)	Experiment	1	2	3	4	5	6
0.1	0	0	0	0	0	0	0
0.5	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002
10.8	0.0049	0.0049	0.0049	0.0049	0.0049	0.0049	0.0049
23.6	0.0108	0.0108	0.0108	0.0108	0.0108	0.0108	0.0108
51.5	0.0236	0.0236	0.0236	0.0236	0.0236	0.0236	0.0236
66.8	0.0306	0.0306	0.0306	0.0306	0.0307	0.0307	0.0306
86.6	0.0397	0.0397	0.0398	0.0397	0.0398	0.0399	0.0397
103.2	0.0474	0.0473	0.0474	0.0474	0.0474	0.0476	0.0472
χ^2		0.001	0.001	0.001	0.002	0.017	0.003
RMSD(%)		0.5	0.4	0.4	0.8	2.2	1.0

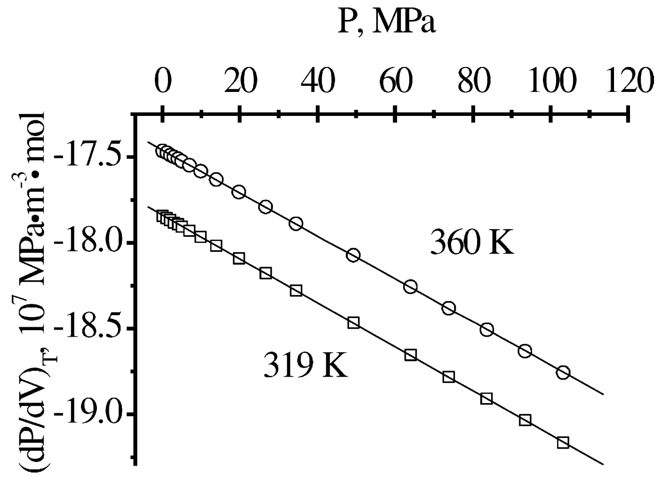

Fig. 7. Thermobaric dependence of isothermal derivative $\left(\frac{\partial P}{\partial V}\right)_T$ at 319 and 360 K.

where V_0 is the molar volume in the reference state, and $A = A'/V_0$ and B are the parameters of the equation of state.

We have calculated A and B parameters for Tait Eq. (7) (see Table III). The confidence intervals δA and δB were accordingly equal to 0.009 and 9 MPa, respectively, with a confidence level equal to 95%. Parameter B is presented as a function of temperature in Fig. 8 for all investigated solutions and pure water. As one can see in Table III, A and B values increase with the C_{60} concentration in water.

According to the statistical analysis of the Tait equation of state [14], parameter A is associated with repulsive potential steepness, and parameter B is associated with the energy of molecular attraction. Parameter A decreases with an increase of repulsive potential steepness, and parameter B increases with an increase of energy of molecular attraction. Thus, taking into account the value of parameter A, we can conclude that repulsive potential steepness for pure water is higher than that for the investigated solutions. At the same time, the molecular attraction energy increases with the addition of C_{60} fullerene into water over the whole investigated range of pressures, temperatures, and concentrations. The last conclusion is in agreement with our previous assumption about molecular interaction energy.

Using the obtained A and B values, we have calculated the isobaric expansivity α_P, isothermal elastic modulus K_T, and the isothermal deviations $T\Delta S, \Delta H$, and ΔU for the investigated C_{60}FAS.

Table III. Calculated A and B Parameters of Tait Equation of State (Eq. (1)) for Pure water andC_{60}FAS with Different Concentrations

T(K)	295	319	342	360
H_2O				
A	0.137			
B(MPa)	296	308	303	293
X_1				
A	0.146			
B(MPa)	351	361	358	348
X_2				
A	0.196			
B(MPa)	460	484	480	465
X_3				
A	0.198			
B(MPa)	525	552	553	538
X_4				
A	0.292			
B(MPa)	867	936	942	927

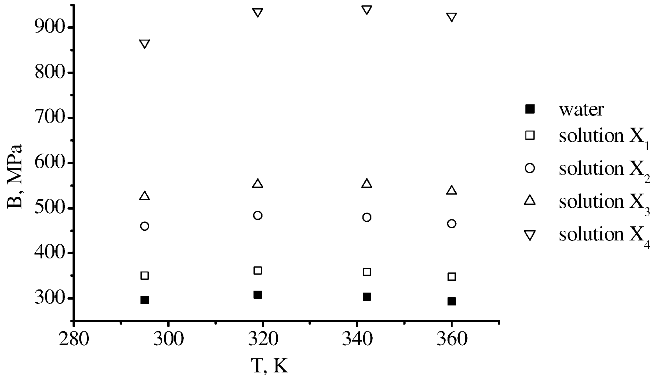

Fig. 8. Tait parameter B as a function of temperature for the C_{60}FAS and pure water.

Thermobaric dependencies of α_P and K_T are described with an RMSD, respectively, equal to 2 and 1%. Thermobaric dependences of isothermal deviations $T\Delta S$, ΔH, and ΔU are described with an RMSD equal to 2, 2 and 2.5%, respectively. Experimental and calculated values of the isothermal deviation of enthalpy as a function of pressure for the C_{60}FAS are represented in Fig. 9.

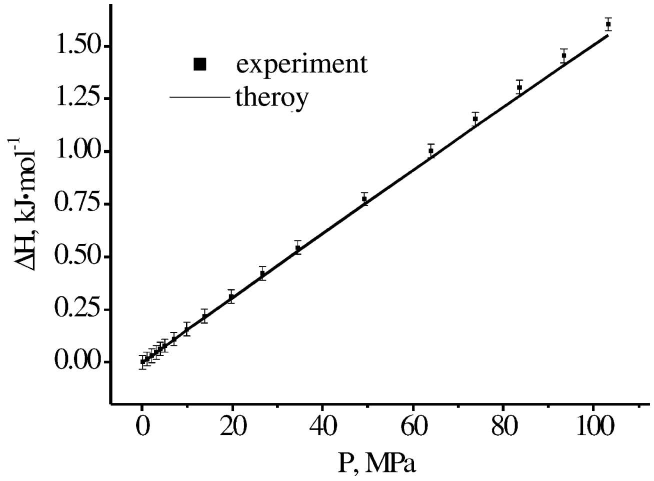

Fig. 9. Isothermal deviation of enthalpy as a function of pressure for the C_{60}FAS at concentration X_4 and $T = 360\,K$.

4. CONCLUSIONS

The following conclusions can be reached:

1. *PVT* data for the C_{60}FAS is described by the Tait equation of state (Eq. (7)) over the whole investigated range of pressures and temperatures with parameter A as a function of concentration and parameter B as a function of temperature and concentration. The obtained equation adequately describes thermobaric dependencies of investigated thermodynamic properties over the whole investigated range of pressures and temperatures.
2. From the analysis of thermodynamic properties, it follows that the energy of molecular attraction in the investigated solutions is an increasing function of concentration over the investigated range of pressures and temperatures.
3. The isothermal equilibrium growth of pressure in the C_{60}FAS leads to the same relative character of isothermal deviations $T\Delta S$, ΔH, and ΔU; the deviation values an increase with the increase of C_{60} concentration in water.
4. The increase of the energy of molecular interaction in the investigated solutions is due to entropy changes of aqueous system.

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