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МАГНИТОКАЛОРИЧЕСКИЙ ЭФФЕКТ И ТЕПЛОЕМКОСТЬ МАГНИТНЫХ ЖИДКОСТЕЙ

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Синтезированы новые магнитные жидкости на основе наночастиц магнетита с использованием смешанного поверхностно-активного вещества (смесь олеиновой кислоты и алкенилянтарного ангидрида), которые были диспергированы в различных дисперсионных средах (первый образец в диалкилдифениле, второй образец в полиэтилсилоксане). Определены физико-химические свойства полученных магнитных жидкостей, такие как: плотность, вязкость, намагниченность насыщения, концентрация магнитной фазы, размер твердой магнитной фазы. Было отмечено, что все синтезированные магнитные жидкости устойчивы в широком диапазоне температур. Установлено, что полученные образцы магнитных жидкостей обладают типичными суперпарамагнитными свойствами. Впервые экспериментально были определены магнитокалорический эффект и удельная теплоемкость синтезированных магнитных жидкостей в интервале температур 288 – 350 К при изменении магнитного поля 0 – 1,0 Тл. Установлено, что полевые зависимости магнитокалорического эффекта имеют классический линейный вид. Определено, что температурные зависимости магнитокалорического эффекта магнитных жидкостей в магнитных полях носят экстремальный характер. Рассчитаны термодинамические параметры намагниченности магнитных жидкостей, а именно изменение энтальпии и изменение энтропии. Температурная зависимость удельной теплоемкости синтезированных образцов магнитной жидкости в нулевом магнитном поле при различных температурах (278 – 350 К) была получена на дифференциальном сканирующем калориметре и оригинальном микрокалориметре. Отмечено, что температурные зависимости теплоемкости магнитных жидкостей в магнитных полях также носят экстремальный характер. Показано, что разница в значениях теплоемкости, полученных в магнитном поле и без него, находится в пределах ошибки эксперимента. Установлено, что экстремальный характер теплоемкости отражается на температурных зависимостях магнитокалорического эффекта.

Ключевые слова: магнитная жидкость, удельная теплоемкость, магнитокалорический эффект

MAGNETOCALORIC EFFECT AND HEAT CAPACITY OF MAGNETIC FLUIDS

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The magnetic fluids based on magnetite nanoparticles were synthesized using mixed surfactants (oleic acid/alkenyl succinic anhydride) dispersed in different carrier media (polyethylsiloxane and dialkyldiphenyl). The physicochemical properties of magnetic fluids (density, viscosity, saturation magnetization, magnetic phase concentration, magnetic core size) were determined. Magnetic fluids are stable in a wide temperature range. All the samples of the magnetic fluids exhibit typical superparamagnetic behavior. The magnetocaloric effect and the specific heat capacity of the magnetic fluids were first direct determined at 288–350 K in a magnetic field of 0–1.0 T. The field dependences of the magnetocaloric effect have a classic linear form. The temperature dependences of the magnetocaloric effect of magnetic fluids in magnetic fields have

an extreme character. Thermodynamic parameters of magnetic fluids (magnetization namely enthalpy/entropy change) were determined. The specific heat capacity of magnetic fluid samples in a zero magnetic field was obtained at different temperatures (at 278–350 K) on a differential scanning calorimeter and on the original microcalorimeter. The temperature dependences of the heat capacity of magnetic fluids in magnetic fields have an extreme character. It was established that the difference in heat capacity values obtained in and without the magnetic field is within the experimental error. The extreme character of the heat capacity is reflected in the magnetocaloric effect temperature dependences.

Key words: magnetic fluid, heat capacity, magnetocaloric effect

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INTRODUCTION

In the last two decades, scientists have intensively studied the magnetocaloric effect (MCE) in various magnetically ordered substances [1, 2]. The essence of the MCE phenomenon is the adiabatic change in the sample temperature under changes in the external magnetic field as a result of the internal energy redistribution between the system of magnetic atoms and the crystal lattice. The intensive studies of MCE have been motivated by its possible medical applications [3, 4] and the possibility to develop a magnetic refrigerator capable of working at room temperature. The literature in this field consists of several thousand articles and reviews [5-8] with a large amount of experimental data. However, scientists have not yet fully understood the MCE physical nature.

In order to solve the fundamental problems of magnetism and solid state physics, it is of special importance to study the magnetocaloric effect in magnetic materials. Thus, we can obtain information about magnetic phase transitions in magnetic materials and about the magnetic state of matter [9]. A magnetocaloric effect changes entropy, heat capacity and thermal conductivity of the magnetic material [10, 11].

In terms of studying magnetothermal properties, the magnetic fluids are very promising objects. The magnetocaloric characteristics of these systems are determined by the nature and size of magnetic phase nanoparticles, the thickness of their adsorption shell, the dispersion medium nature [12, 13]. The MCE and heat capacity, at the same time, can provide us with a lot of information but, among the thermodynamic characteristics of magnetic fluids, they are the least studied ones. The magnetic fluids are unique representatives of nanoscale systems. They combine the properties of a liquid and a magnetic material.

All this makes it undoubtedly important, both for the fundamental science and for developing various functional devices, to conduct experimental studies of the magnetocaloric effect and the heat capacity of magnetic colloids of different nature.

RESEARCH METHODS

The following commercial grade components from Acros Organics were used: iron sulfate ($FeSO_4 \cdot 7H_2O$, 99%), iron chloride ($FeCl_3 \cdot 6H_2O$, 98%), aqueous ammonia (NH_4OH, 25%), oleic acid (97%), and alkenylsuccinic anhydride ($C_{76}H_{145}O_3$, 80%).

The magnetite nanoparticles were synthesized by coprecipitation of the iron (II) sulfate and iron (III) chloride salts with an excess amount of the water ammonia solution (NH_4OH) in a thermostatically controlled vessel at a temperature of 298 K. Similar methods are reported in work [14]. The obtained suspension was repeatedly washed with distilled water until the specific electrical conductivity of the flush water (1.77 μSm/cm) was reached as reported in [15]. The crystal structure of the magnetite particles was determined by the X-Ray analysis on a multifunctional X-ray diffractometer D8 Advance (Bruker-AXS, Germany) (diffraction at small angels of 2θ = 1-100°). The particle size was measured by the Zetasizer nano ZS (Malvern Instruments Ltd, UK). The analysis results have shown that the magnetite crystals have a spinel structure (JCPDS Card 19-0629) and that the size of most of the magnetite crystals is in the range of 10-20 nm [16].

Polyethylsiloxane (PES-4^{tm}) and dialkyldiphenyl (Alkaren D24S^{tm}) were used as dispersion media (DM). Polyethylsiloxane was chosen because of its low saturated vapor pressure, low melting point,

good dielectric, and hydrophobic properties, low temperature viscosity coefficient and low surface tension [15]. Besides, it has good thermal conductivity and thermal oxidation stability. Such polyethylsiloxane-based liquid can act as a carrier medium of magnetic fluids in liquid sealing, especially at low temperatures and in vacuum conditions. Dialkyldiphenyl has a high thermal oxidation stability, low vapor pressure, low viscosity, good tribological features and is resistant to hydrolysis. Moreover, it is nontoxic and inert.

The magnetic fluids (MF) were prepared by stabilizing the magnetite nanoparticles in the dispersion medium. The freshly prepared magnetite was first centrifuged in order to remove water. The surface of the particles was stabilized with a surfactant monomolecular adsorbing layer and then the stabilized magnetite was peptized in a dispersion medium at T = 85 °C for 6-10 hrs. A mixture of oleic acid and alkenylsuccinic anhydride [15] has been used as a surfactant. This mixed surfactant is expected to expand the range of magnetic fluid applications. The composition of the samples and its properties are given in Table 1.

Table 1

Composition and properties of the synthesized magnetic fluids samples (T=296 K)

***Таблица 1*. Состав и свойства образцов синтезированных магнитных жидкостей (T=296 K)**

Sample	**MF 1**	**MF 2**
Composition MF	Oleic acid/Alkenyl succinic anhydride (2:8)[b] Alkaren D24S	Oleic acid/Alkenyl succinic anhydride (2:8)[b] PES-4
Density (g cm^{-3})	1.23	1.17
Viscosity (Pa·s)	0.54	0.17
Saturation magnetization[a] (kA m^{-1})	12.9	13.5
Magnetic concentration[a] (% vol.)	2.9	3.8
Magnetic core size[a] (nm)	13.0	15.2

Notes: [a] the data was presented in work [15],
[b] in brackets is component ratio.
Примечания: [a] данные представлены в работе [15],
[b] в скобках указано соотношение компонентов

The magnetic measurements were made using a vibrating sample magnetometer Lake Shore 7407 (Lake Shore Cryotronics, USA) [15]. In [15], experimental data on magnetic measurements of the sample **MF 1** are presented. In particular, it is noted that samples of magnetic fluids exhibit typical superparamagnetic behavior, with no magnetic hysteresis on the magnetization curves.

The heat capacity in zero magnetic fields was measured with the DSC 204 F1 Phoenix (NETZSCH, Germany) at the temperatures of 278-320 K. The heat capacity experimental uncertainty was 1.5%. Every experiment was repeated five times. Besides, the heat capacity in magnetic fields was measured by a special microcalorimeter [17]. Research was done in the temperature range of 288-350 K and in magnetic fields of 0-1.0 T. The heat capacity experimental uncertainty was 2%. It is worth noting that the magnetic fluid heat capacity values obtained by the DSC 204 F1 calorimeter agree with the data obtained on the special microcalorimeter.

The magnetocaloric effects (MCE) of magnetic fluids were studied using a special microcalorimeter [17]. The experimental uncertainty of the MCE measurements that were repeated five times did not exceed 2%. The reliability of the method used was checked by calibrating the microcalorimeter with metallic gadolinium (the chemical purity was 98%) as in [17].

The amount of the heat Q_{MCE} (J/g), which was allocated when the magnetic field was switched on was calculated by Equations (1):

$$Q_{MCE} = Q_J (\Delta T/\Delta T_J), \quad (1)$$

where Q_J (J/g) is the Joule heat, injected in the calorimetric experiment, ΔT_J (K) is the temperature change of calorimetric system as a result of injecting the Joule heat, ΔT (K) is the temperature change in the calorimetric system as a result of changing magnetic field (MCE). The equation of heat balance [17] has the form (2):

$$Q_{MCE} = m_{(MF)}\, C_{p(MF)}\, \Delta T_{MCE}, \quad (2)$$

where ΔT_{MCE} (K) is the temperature change that is MCE, $m_{(MF)}$ (g) and $C_{p(MF)}$ (J/g K) are the mass and heat capacity of a magnetic fluid. The enthalpy change, ΔH (J/mol), in the magnetic material resulting from the changes in the magnetic field was determined from the experimental values of Q_{MCE}.

We calculated the values of changes in the entropy of the studied molecular magnetics in magnetic field, ΔS (J/g K), using the C_p values in zero fields by Eq. (3):

$$\Delta S = -C_p\, \Delta T_{MCE}/T \quad (3)$$

Here, C_p is the specific heat capacity, ΔT_{MCE} is the magnetocaloric effect; T is the absolute temperature.

RESULTS AND DISCUSSION

Since the heat capacity of a heterogeneous system is equal to the sum of the heat capacities of its components and depends on their concentration in the system, it can be concluded that the relation of the specific heat capacity of a magnetic fluid and the heat capacity of its components can be written as (4):

$$C_{p(MF)} = C_{p(solid)}\, w_{(solid)} + C_{p(DM)}\, w_{(DM)}, \quad (4)$$

where $C_{p(solid)}$, $C_{p(MF)}$ and $C_{p(DM)}$ (J/g K) are specific heat capacities of the solid phase, magnetic fluid and dispersion medium, respectively, $w_{(solid)}$ and $w_{(DM)}$ (g) are the mass fractions of the solid phase and dispersion medium in a magnetic fluid, respectively.

Equation (4) does not account for the surfactant heat capacity as the magnetic fluid has a very small amount of it.

Fig. 1 and Table 2 shows the heat capacities of magnetic fluid samples and their components at 296 K (B = 0 T). The heat capacities of the components were taken from literature sources [18-20] and obtained on the calorimeter DSC 204 F1.

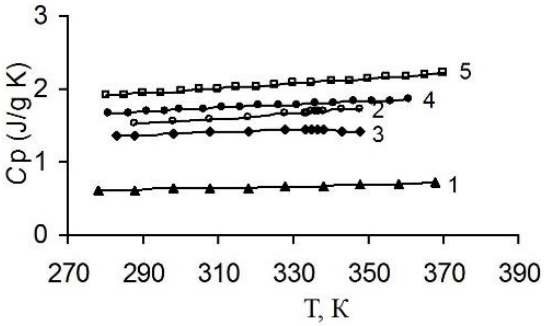

Fig. 1. Temperature dependence of the specific heat capacity of magnetic fluid samples and their components: (1) - magnetite [18], (2) - MF 1, (3) - MF 2, (4) - polyethylsiloxane (PES-4), (5) - dialkyldiphenyl (Alkaren D24S)

Рис. 1. Температурная зависимость удельной теплоемкости образцов магнитной жидкости (МЖ 1 и МЖ 2) и их компонентов. (1) – магнетит [18]; (2) – МЖ 1; (3) – МЖ 2; (4) – ПЭС-4; (5) – Алкарен D24S

The polynomial equations to describe the dependence $C_p = f(T)$ are as follows:

$$C_p \text{ (Alkaren D24S)} = 0.00000004x^3 - 0.00004261x^2 + 0.01741620x - 0.57457015 \quad (5)$$

The correlation coefficient of the fitting $R^2 = 0.998$.

$$C_p \text{ (PES-4)} = -0.00001044x^2 + 0.00926473x - 0.13271892 \quad (6)$$

The correlation coefficient of the fitting $R^2 = 0.836$.

$$C_p \text{ (\textbf{MF 1})} = -0.00000058x^3 + 0.00010250x^2 - 0.00173865x + 1.53213102 \quad (7)$$

The correlation coefficient of the fitting $R^2 = 0.940$.

$$C_p \text{ (\textbf{MF 2})} = 0.00000038x^3 - 0.00008815x^2 + 0.00622446x + 1.29184727 \quad (8)$$

The correlation coefficient of the fitting $R^2 = 0.812$

Table 2

Specific heat capacities of the synthesized magnetic fluids samples and their components (T=296 K, B=0 T)

***Таблица 2.* Удельные теплоемкости синтезированных образцов магнитных жидкостей и их компонентов (T=296 K, B=0 Тл)**

Sample	C_p [a] (J/g K)
MF 1	1.54±0.03
Dialkyldiphenyl (Alkaren D24S)	1.83±0.03
MF 2	1.39±0.02
Polyethylsiloxane (PES-4)	1.69±0.03 (1.68 [19, 20])
Magnetite (Fe_3O_4)	0.64 [18]

Note: [a] the heat capacity experimental uncertainty by a special microcalorimeter was 2%

Примечание: [a] погрешность экспериментального определения теплоемкости с помощью микрокалориметра была 2%

By analyzing equation (4), we can conclude that the heat capacity of magnetic fluids depends on the nature of the components and, consequently, on their specific heat capacity. A main contribution to the heat capacity is made by the dispersion medium. For example, at T = 296 K sample **MF 1** based on dialkyldiphenyl ($C_{p(DM)}$ = 1.83±0.03 J/g K) has high specific heat capacity ($C_{p(MF1)}$ = 1.54±0.03 J/g K) compared to sample **MF 2** ($C_{p(MF2)}$ = 1.39±0.02 J/g K) based on polyethylsiloxane ($C_{p(DM)}$ = 1.69±0.03 J/g K). Such dependence is observed in the whole temperature range that was studied (Fig. 1). However, under the influence of a magnetic field (at $B \neq 0$ T), the dependence is changing.

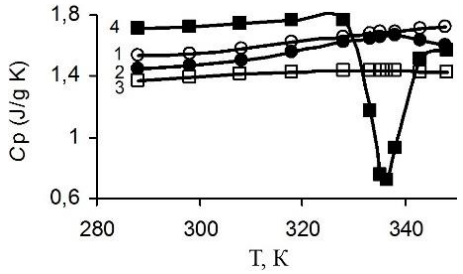

Fig. 2. Temperature dependence of the specific heat capacity of magnetic fluid samples. Samples MF 1 and samples MF 2 in zero magnetic field (B=0 T) and in magnetic field (B=1.0 T) (data were measured by microcalorimeter). (1) – C_p(MF 1) at B=0 T; (2) – C_p(MF 1) at B=1.0 T; (3) – C_p(MF 2) at B=0 T; (4) – C_p(MF 2) at B=1.0 T

Рис. 2. Температурная зависимость удельной теплоемкости образцов МЖ 1 и МЖ 2 магнитной жидкости в нулевом поле (B=0 Тл) и в магнитном поле (B=1,0 Тл) (данные получены на микрокалориметре). (1) – C_p(МЖ 1) при B=0 Тл; (2) – C_p(МЖ 1) при B=1,0 Тл; (3) – C_p(МЖ 2) при B=0 Тл; (4) – C_p(МЖ 2) при B=1,0 Тл

The specific heat capacity of samples of **MF 1** and **MF 2** in a zero magnetic field, were obtained at different temperatures on a differential scanning calorimeter DSC 204 F1 Phoenix (NETZSCH, Germany) (the heat capacity measurement error was 1.5%) and

on the original microcalorimeter (measurement error heat capacity was 2%). In results was established that the difference in heat capacity values is within the experimental error.

In the zero magnetic fields, the heat capacity of both samples rises with the temperature increase (Fig. 2). If the magnetic field induction is equal to 1.0 T (B = 1.0 T) in the temperature range of 320-350 K (Fig. 2), the temperature dependences have maxima. The magnetic field has effect on both samples (Fig. 2). Moreover, when dialkyldiphenyl is replaced by polyethylsiloxane in a magnetic fluid (transition from **MF 1** to **MF 2**), the specific heat capacity of the sample **MF 1** decreases, and the sample **MF 2** increases with the appearance of an extreme at 330-340 K. The difference in the heat capacity behavior is caused by the differences in the nature and structure of the dispersion media (dialkyldiphenyl has a conjugated π-system, while polyethylsiloxane has a line chain structure) [19] although the exact nature of the differences is currently unclear.

Fig. 3 shows the experimentally obtained field dependences of the magnetocaloric effect of sample **MF 1** at 308 K. The linear equations to describe the dependence $\Delta T_{MCE} = f(B)$ are as follows:

$$\Delta T_{MCE}\,(K) = 0.00972 \cdot B, \quad (9)$$

$$-\Delta T_{MCE}\,(K) = 0.00972 \cdot B. \quad (10)$$

The correlation coefficient of the fitting $R^2 = 0.998$.

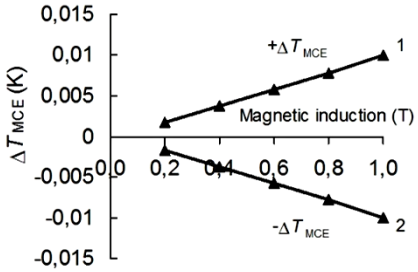

Fig. 3. Magnitudes of positive (1) and negative (2) magnetocaloric effects in sample **MF 1** as functions of magnetic induction at 308K. The experimental uncertainty of the MCE measurements was 2%

Рис. 3. Величина положительного (1) и отрицательного (2) магнитокалорического эффекта образца **МЖ 1** в зависимости от индукции магнитного поля при 308 К. Погрешность в определении МКЭ 2%

Positive values of the MCE, obtained when the magnetic field is switched on (heat release), are completely the same as the negative values of the MCE, obtained when the magnetic field is turned off (heat absorption). It should be noted that the magnitude of the MCE of magnetic fluid with a volume concentration of the magnetic phase of 2.9% (sample **MF 1**) at 1.0 T is 0.008 K. Earlier, it was established [21] that the MCE increases linearly with increasing concentration of the magnetic phase. This is due, firstly, to an increase in the magnetization of a magnetic fluid with increasing concentration of magnetite. Secondly, an increase in the share of magnetite $C_{p(MF)}$ = 0.64 J/g K [18] at 293 K leads to a decrease in the heat capacity of the magnetic fluid as a whole and, accordingly, increases the MCE (see equation 4).

The temperature dependences of MCE in the studied magnetic fluid samples are shown in Fig. 4. Generally, the temperature dependence of MCE in magnetic fluid repeats the type of temperature dependence of specific heat Q_{MCE} (Q_{MCE} not given here). With increasing magnetic field induction, the MCE values of the sample **MF 2** increase (Fig. 4). In the temperature range of 330-340 K, a maximum is observed on the curves, which also increases with increasing magnetic induction.

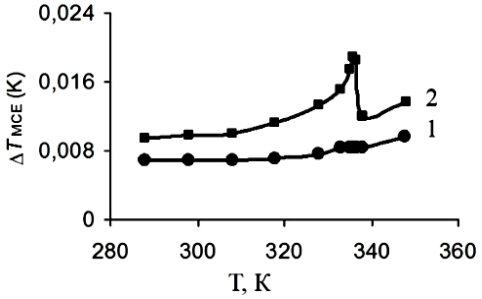

Fig. 4. Temperature dependence of the magnetocaloric effect of magnetic fluid samples **MF 1** (1) and **MF 2** (2) at magnetic field B=1.0 T. The experimental uncertainty of the ΔT_{MCE} measurements was 2%

Рис. 4. Температурная зависимость магнитокалорического эффекта образцов **МЖ 1** и **МЖ 2** с индукцией магнитного поля B=1,0 Т. Погрешность в определении $\Delta T_{МКЭ}$ 2%

The MCE for sample **MF 2**, at temperatures above 310 K, is significantly higher than for **MF 1** (Fig. 4) and is associated with higher magnetization and concentration of magnetic nanoparticles (Table 1). For the sample **MF 2** based on polyethylsiloxane, the extreme dependence of MCE in the temperature range of 330-340 K is related to the extreme dependence of C_p at the same temperatures, which is confirmed by the analysis of equation (1). It should be noted that for both samples in the temperature range of 298-330 K there is a slight decrease in the MCE values. At the temperatures > 340 K, a sharp increase in the MCE is observed, which is reflected in the high magnetic fields.

Fig. 5 shows the temperature dependences of the magnetocaloric effect of magnetic phase in magnetic fluid (sample **MF 1**). It is noteworthy that the magnetocaloric effect of magnetite in a magnetic fluid exceeds the value of the MCE of the magnetic fluid (ΔT_{MCE} (**MF 1**) = 0.007 K and ΔT_{MCE} (magnetite in **MF 1**) = 1.2 K at 308 K). This can be explained by the difference in the heat capacities of magnetite and magnetic fluid and their quantity per unit volume.

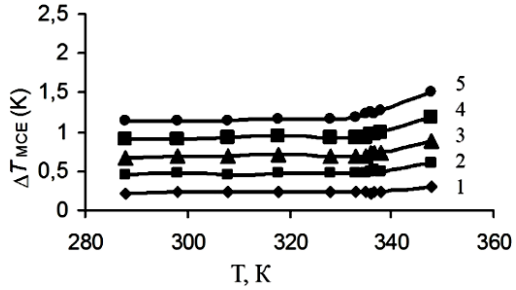

Fig. 5. Temperature dependence of the magnetocaloric effect of magnetite in a magnetic fluid sample **MF 1.** 1 – 0.2 T, 2 - 0.4 T, 3 - 0.6 T, 4 - 0.8 T, 5 - 1.0 T

Рис.5. Температурная зависимость магнитокалорического эффекта магнетита в составе образца **МЖ 1** в магнитном поле. 1 – 0.2 T, 2 - 0.4 T, 3 - 0.6 T, 4 - 0.8 T, 5 - 1.0 T

The temperature dependences of the calculated enthalpy changes ΔH (J/mol) and changes in the entropy ΔS (J/kg K) of the studied magnetic fluid samples in the magnetic field are shown in Table 3. ΔH and ΔS of magnetic phase in magnetic fluid (sample **MF 1**) are shown in Table 3 too. These values are the direct parameters for estimating the cooling capacity of sample.

Table 3

The temperature dependences of the calculated entropy and enthalpy changes of samples (*B* = 1.0 T)

***Таблица 3.* Температурные зависимости рассчитанных изменений энтропии и энтальпии образцов (*B* = 1.0 T)**

T, K	Δ*S*, J/kg K			Δ*H*, J/mol	
	Fe_3O_4 (from **MF 1**)	**MF 1**	**MF2**	Fe_3O_4 (from **MF 1**)	**MF2**
288	5.9	0.035	0.045	0.0074	8.7
298	5.9	0.035	0.046	0.0076	9.1
308	5.8	0.035	0.047	0.0078	9.3
318	5.9	0.036	0.050	0.0081	10.5
328	5.9	0.038	0.057	0.0083	12.7
333	5.9	0.040	0.064	0.0085	14.2
335	6.1	0.042	0.074	0.0088	16.5
336	6.4	0.043	0.080	0.0093	17.8
336.5	6.5	0.045	0.078	0.0095	17.4
338	6.7	0.046	0.055	0.0098	11.9
348	8.6	0.049	0.064	0.0129	12.9

CONCLUSION

In this work, we have synthesized magnetic fluids based on magnetite nanoparticles using mixed surfactants (oleic acid/alkenyl succinic anhydride) dispersed in different carrier media (polyethylsiloxane and dialkyldiphenyl). All the samples of the magnetic fluids behave as superparamagnetic. The magnetocaloric effect and the heat capacity of the magnetic fluids were determined by the microcalorimetric method at 288-350K in a magnetic field of 0-1.0 T.

The specific heat capacity magnitude of magnetic fluids is determined by the heat capacity values of its components. The temperature dependence of the heat capacity in the magnetic field is of extreme nature.

The field dependences of the MCE are linear. The MCE values increase linearly with the magnetic field growth. The extreme character of the heat capacity is reflected in the MCE temperature dependences. When the dispersion medium is replaced, the character of the MCE temperature dependence changes, i.e. when polyethylsiloxane is replaced with dialkyldiphenyl, the extreme on the temperature dependence disappears.

It should be noted that the observed jumps on the temperature dependences of the MCE should be taken into account when designing various devices using magnetic magnetite fluid.

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