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Letter to the Editor

Confirmation of water mechanism in zeolite electrorheological fluid by dielectric spectroscopy

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ABSTRACT

Zeolite electrorheological(ER) liquids with different amounts of adsorbed water were measured by dielectric spectroscopy, and the dielectric parameters of every system were fitted by Cole-Cole equation. The permittivity of the dispersed particle was found to increase with adsorbed water increasing, however, the dielectric increment of the ER liquid was independent on the adsorbed water. Considering the relationship between interfacial polarization and ER effect, the previous permittivity mechanism of adsorbed water was confirmed to be unsuitable to zeolite ER liquids. Based on analyzing the relaxation times of different systems, the dielectric loss mechanism was proposed to explain the positive effect of adsorbed water on the ER behavior of zeolite/oil suspension.

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1. Introduction

Electrorheological(ER) liquids, which consist of polarizable particles or liquid crystal materials suspended in an insulating liquid, have been researched over sixty years [1,2]. When an external electric field with several kilovolts per millimeter is applied, ER liquids can rapidly change from a fluid-like state to a solid-like state. The ER effect is commonly considered because the dispersed materials acquire electric moments under electric field, and then attract each other into chain under the influence of the electrical forces between these induced moments. As an important kind of ER material, zeolite ER liquids have been intensively researched recently [3–5]. Some factors such as lattice type, volume fraction of particle, and external electric field have been studied to uncover the mechanisms in the ER effect. In particular, the adsorbed water has been found to positively strengthen the ER behaviors of zeolite/oil suspensions [6]. For general ER liquids, the function of the adsorbed water was primarily assumed to increase the permittivity of the dispersed particle, which in turn resulted in a strengthening of particle interaction [7,8]. Another hypothesis is that the adsorbed water could stick the particles together due to the property of high surface tension of water [9,10]. In the present work, however, we found the above two mechanisms are deficient to the zeolite ER liquids. Basing on the dielectric relaxation analysis, we studied the effect of the adsorbed water on the interface polarization of the zeolite ER liquids, and contributed the dielectric loss mechanism to the experimental results.

2. Experimental

4A zeolite (LTA) was commercially available from Sigma Chemical Co. The average particle size is around 4 μm, the density is about 2.07 g cm^{-3}. A thermogravimetric analysis was carried out to measure the water content of the sample, and the saturation content of adsorbed water inside zeolite pores is about 17%. By means of controlling the heating temperature and time, three kinds of LTA with different water content were obtained: LTA_1 (0% water), LTA_2 (7% water) and LTA_3 (14% water). The three kinds of LTA were respectively dispersed in silicone oil with particle volume fraction from 0.03 to 0.14. The silicone oil was dehydrated with molecular sieves before use in order to get rid of any traces of water.

Dielectric measurements of LTA/silicone oil suspensions were carried out by Agilent 4192A LF impedance analyzer from Hewlett Packard in the frequency range of 40 Hz to 110 MHz. The amplitude of the applied alternating field was 50 mV, and the measurement temperature was 25 ± 1 °C. The dielectric cell consists of parallel stainless steel electrodes, whose constant and stray capacitance were determined by using several standard liquids. Data obtained were all subjected to certain corrections for errors arising from residual inductance due to the cell assembly. The permittivity of water, alcohol, and atmosphere were measured at 25 ± 1 °C as a valuation of the correction of dielectric measurement, the values are $\varepsilon_{H_2O} = 80.9$, $\varepsilon_{C_2H_5OH} = 25.3$, and $\varepsilon_{air} = 1.00$ respectively. The results agree with the

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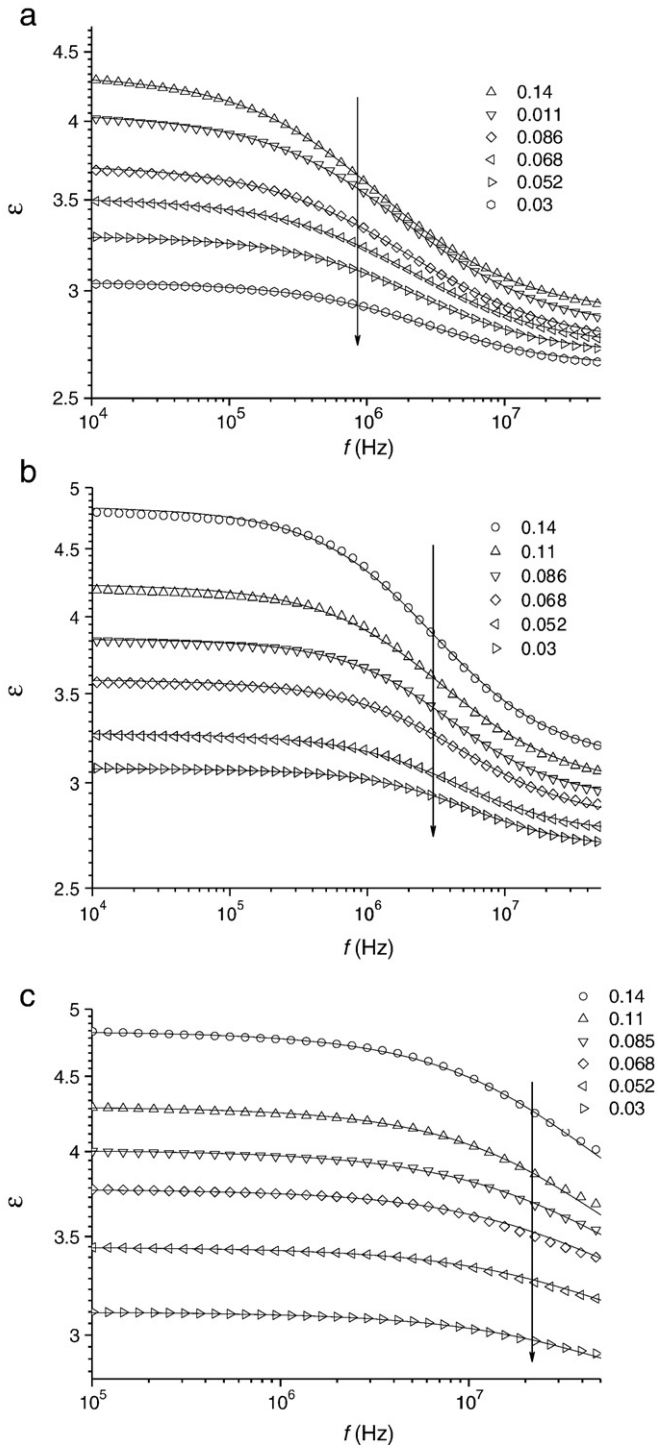

Fig. 1. The dielectric constant as a function of the applied electrical frequency for LTA_1 (a), LTA_2 (b) and LTA_3 (c) dispersed in the silicone oil in different volume fractions.

standard values, which indicate that the corrections of systemic errors are suitable.

3. Results and discussion

Fig. 1 a, b and c shows the frequency dependence of the permittivity ε for three kinds of LTA/silicone oil suspensions with different volume fractions, respectively. A distinct relaxation (arrow positions) can be observed in every figure, moreover, the relaxation frequency increases with the increment of adsorbed water content. In our previous works [11], the dielectric relaxation of LTA ER liquids was referred to the interfacial polarization, which has been considered as the key factor to the ER effect. In order to obtain the effect of adsorbed water on the dielectric properties of ER liquid, the Cole–Cole equation is used to extract the dielectric parameters from the dielectric spectra (Fig. 1 a, b and c)

$$\varepsilon = \varepsilon_h + \frac{\Delta\varepsilon}{1 + (j\omega\tau_0)^{1-\alpha}} \tag{1}$$

where ε is the collective permittivity of the liquid suspension, $\Delta\varepsilon = \varepsilon_l - \varepsilon_h$ dielectric increment, subscripts l, h indicate the low and high frequency, τ_0 relaxation time $(=1/2\pi f_0)$, $1-\alpha$ the parameter indicating the width of the distribution of relaxation time. According to Eq. (1), the dielectric parameters of the LTA/Silicone-oil suspensions with different water amount were fitted, and the main results are listed in Table 1. The best-fit results were displayed in Fig. 1 simultaneously, which are in good agreement with the experimental data. Among the parameters in the Cole–Cole equation, τ_0 and $\Delta\varepsilon$ are considered as important factors to affect ER activity [12]. The τ_0 value is related to the rate of interfacial polarization, and $\Delta\varepsilon$ displays the degree of interfacial polarization. As the shorter τ_0 within adequate rang and the bigger $\Delta\varepsilon$ are applied, the higher stress enhancement applied by an electric field is achieved.

Water-bridge mechanism considers that water molecules could stick the particles together due to the high surface tension of water. Different from other particle in ER liquid, however, zeolite can confined the water into the structural framework. Because of the special absorption way, ER liquids using zeolite particle as dispersed phase are thermally more stable than other wet-base ER liquids. According to the thermogravimetric analysis, the saturation content of water in LTA zeolite is about 17%. Usually, the water as additive in zeolite ER liquid was below 10%. So the adsorbed water hardly exists on the surface of zeolite particle to form the bridge between the particles. In order to confirm the applicability of the permittivity mechanism of water to zeolite ER liquid, a mix equation is used to calculate the permittivity of LTA particle in ER liquid [13]

$$\varepsilon_l = \phi\varepsilon_p + (1-\phi)\varepsilon_m \tag{2}$$

where ε_m is the permittivity of disperse medium, ε_p is the permittivity of the dispersed particle. As the disperse medium of LTA ER liquids, the permittivity of silicone oil is equal to 2.61, and independent on the concentration of dispersed phase and the amount of adsorbed water.

Table 1
Dielectric parameters of three kind of LTA ER liquid with different volume fractions.

Volume Fraction	LTA_1				LTA_2				LTA_3			
	ε_l	$\Delta\varepsilon$	$\tau_0\times10^8$/s	Fitting Degree %	ε_l	$\Delta\varepsilon$	$\tau_0\times10^8$/s	Fitting Degree %	ε_l	$\Delta\varepsilon$	$\tau_0\times10^8$/s	Fitting Degree %
0.14	4.42	1.47	13.0	99.3	4.58	1.51	6.5	98.6	4.64	1.49	0.45	99.1
0.11	4.05	1.27	10.5	99.2	4.12	1.26	5.3	98.9	4.23	1.24	0.38	99.3
0.085	3.72	0.99	9.4	98.5	3.81	0.95	4.5	98.5	3.85	1.03	0.29	98.8
0.068	3.51	0.80	8.3	99.2	3.57	0.79	3.7	99.0	3.59	0.81	0.29	98.8
0.052	3.29	0.60	7.5	99.1	3.34	0.57	3.8	99.2	3.37	0.58	0.28	99.2
0.030	3.00	0.41	6.4	98.7	3.03	0.40	3.0	98.7	3.05	0.43	0.26	99.0

Table 2
The permittivity of LTA particle in three kind of LTA ER liquid with different volume fractions.

Volume Fraction	ε_p		
	LTA_1	LTA_2	LTA_3
0.14	15.5	16.7	17.1
0.11	15.7	16.3	17.3
0.085	15.7	16.7	17.2
0.068	15.8	16.7	17.0
0.052	15.7	16.6	17.0
0.030	15.6	16.6	17.3

Based on the fitted dielectric parameters in Table 1, ε_p of LTA ER liquids with different volume fractions and water amounts are calculated from Eq. (2) and listed in Table 2. As seen in the results, the permittivity of LTA particle is increased with the adsorbed water increasing.

The permittivity of dielectric material consists of four kinds of polarizations: electronic, atomic, the Debye and the interfacial polarization (the Wagner-Maxwell polarization). Meanwhile, the interfacial polarization has been concluded to be responsible to the ER effect [14]. So the mechanism of adsorbed water in LTA ER liquids should be further demonstrated by means of analyzing the effect of adsorbed water on the partial permittivity originated from the interfacial polarization. Considering the correspondence between the dielectric relaxation in Fig. 1 and the interfacial polarization of LTA ER liquids, the $\Delta\varepsilon$ is used as a token parameter to analyze the effect of water on the interfacial polarization. As seen in Fig. 2, the dehydrated and hydrated LTA fluids with same volume fraction show almost equal dielectric increment, which means the adsorbed water does not change the degree of interfacial polarization. Inside the pore of LTA, there are two kinds of optional lattice sites for cations locating. One is active site, in which the cations can conquer the electrostatic attraction of electronegative framework and move directionally along the main channel of zeolite. The transferring motion of cations is contributed to the interfacial polarization of LTA fluid. The other is non-active site, where the cations are tightly bonded and only vibrate in a finite region. Because of the constant dielectric increment with adsorbed water increasing, it can be concluded that the adsorbed water cannot activate the cations on the non-active sites, and there is no difference between the amounts of the cations responsible to interfacial polarization before and after adsorbed water. Therefore, the permittivity mechanism is not suitable to explain the effect of adsorbed water on the ER effect of zeolite fluid.

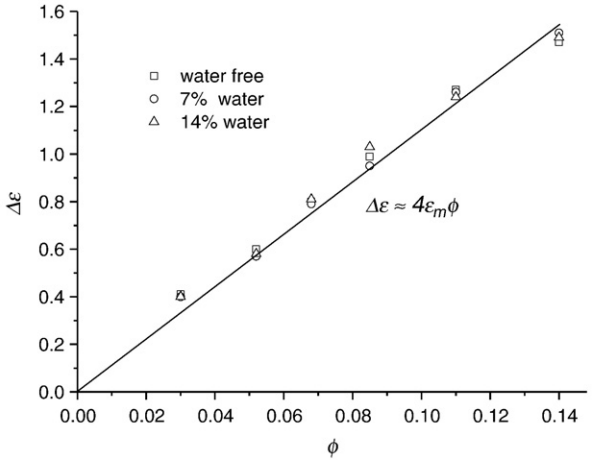

Fig. 2. The comparison of dielectric increment of three kinds of LTA/Silicone-oil suspensions with different volume fraction.

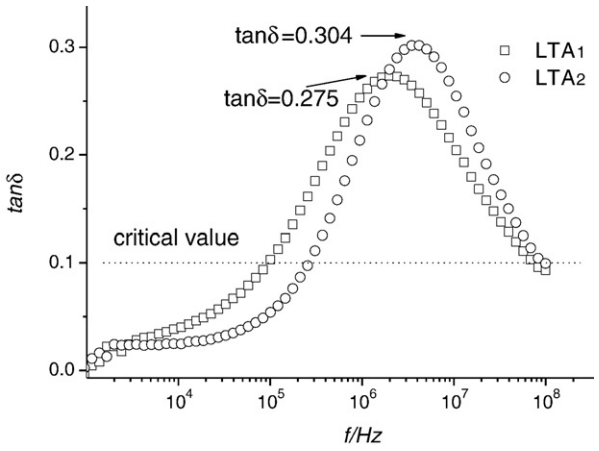

Fig. 3. The frequency dependence of the dielectric loss tangent of the dehydrated and the hydrated LTA ER liquid.

As seen in Table 1, LTA_2 ER liquids display shorter relaxation time than LTA_1.When the water is adsorbed into the pore of particle, the negatively charged framework is coordinated by water molecules with hydrogen bond, leading to a weakened interaction with sodium ions. As a result, the mobility of sodium ions on active sites is increased, and the amount of polarized cations relative to the interfacial polarization is not changed. Based on above analyses, the dielectric loss mechanism is proposed to clarify the effect of water on zeolite ER liquid. For ER effect, two dynamic processes are emphasized. Firstly, the particle can be polarized under electric field, in which the dielectric increment is dominant. The adsorbed water molecules do not change the dielectric increment of zeolite particles in this paper. Therefore, the effect of adsorbed water is not considered in first step. Secondly, the polarized particle must possess the turning ability in oil medium to align along the direction of the electric field. This step is usually determined by the particle dielectric loss, which distinguishes the ER particle from non-ER particle. In other words, both the ER particle and non-ER particle could be polarized under an electric field, however, the ER particle could re-orientate along the electric field direction, building the fibrillated bridges between two electrodes. The dielectric loss mechanism indicates that the suspended particles can become ordered under an electric field only when the maximum value of the dielectric loss tangent is larger than 0.1[15]

$$\tan\delta = \varepsilon'' / \varepsilon' \tag{3}$$

$$\varepsilon'' = \frac{\kappa - \kappa_l}{\omega \cdot \varepsilon_0} \tag{4}$$

where δ is the dielectric loss tangent, ε'' and ε' are the real and imaginary part of complex permittivity, respectively, ε_0 is the permittivity of vacuum, κ is conductivity. Fig. 3 is the frequency dependence of the dielectric loss tangents of LTA_1 and LTA_2 ER liquid, both of maximum tanδ are larger than 0.1. It explains that the dehydrated LTA ER liquid can display ER effect. Moreover, the hydrated LTA ER liquid possesses higher value of $\tan\delta_{max}$. It indicates that the hydrated LTA ER liquid possesses better turning ability than dehydrated. As a result, the adsorbed water can obviously improve the ER effect of LTA ER liquid.

4. Conclusion

In conclusion, we have confirmed the water mechanism in zeolite ER liquid by means of the dielectric spectroscopy. The previous permittivity mechanism and water-bridge mechanism have been

confirmed to be unsuitable to zeolite ER liquids. With the adsorption of water, the mobility of cations inside pore and on the surface of zeolite particle is increased. As a result, the increase in the dielectric loss improves the turning ability of zeolite particle in silicone oil medium under electric field.

Acknowledgments

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References

[1] T. Hao, Adv. Colloid Interface Sci. 97 (2002) 1.
[2] K. Kim, D. Stroud, X.T. Li, Phys. Rev. E 71 (2005) 031503.
[3] H.J. Choi, M.S. Cho, K.K. Kang, W.S. Ahn, Micropor. Mesopor. Mat. 39 (2000) 19.
[4] Y. Tian, Y.G. Meng, S.Z. Wen, Mater. Lett. 57 (2003) 2807.
[5] M.S. Cho, H.J. Choi, W.S. Ahn, Langmuir 20 (2004) 202.
[6] C. Gehin, J. Persello, J. Colloid Interface Sci. 273 (2004) 658.
[7] Y.F. Deinega, G.V. Vinogradov, Rheol. Acta 2321 (1984) 636.
[8] H. Uejima, Jpn. J. Appl. Phys. 11 (1972) 319.
[9] J.E. Stangroom, Phys.Techn. 142 (1983) 290.
[10] C. Gehin, J. Persello, D. Charraut, B. Cabane, J. Colloid Interface Sci. 273 (2004) 658.
[11] W. Zhou, K.S. Zhao, Colloids and Surfaces A. 317 (2008) 10.
[12] H. Block, J. Kelley, Langmuir 6 (1990) 6.
[13] L. Marshall, F. Zukoshi, J.W. Goodwin, J. Chem. Soc. Faraday Trans. 85 (1989) 2785.
[14] T. Hao, A. Kawai, F. Ikazaki, Langmuir 14 (1998) 1256.
[15] T. Hao, A. Kawai, F. Ikazaki, Langmuir 15 (1999) 918.