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Impedance and modulus spectroscopic studies on $(CuI)_{100-x}$–$(Ag_2SO_4)_x$ ($0 \leqslant x \leqslant 60$) mixed system

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The frequency-dependent conductivity, σ_ω measurements on $(CuI)_{100-x}$–$(Ag_2SO_4)_x$ ($0 \leqslant x \leqslant 60$) mixed system in the frequency range 1 Hz–65.5 kHz and over the temperature range 293–403 K have been carried out. These studies have illustrated similarities in the behaviour of the present system and the other fast ionic solid systems which are generally found to obey the Jonscher's universal power law, $\sigma_{\text{a.c.}}(\omega) = \sigma_0 + A\omega^n$, where $\sigma_{\text{a.c.}}(\omega)$ is the conductivity at frequency ω, σ_0 is the limiting zero frequency conductivity or d.c. conductivity and A and n are fitting parameters. The value of n decreases with increasing temperature and A and σ_0 increase with temperature (n is a temperature-dependent frequency exponent, A is a frequency-independent and temperature-dependent parameter). These results appear to suggest a mechanism of fast ion conduction due to the presence of well-defined pathways. The strong low-frequency dispersion observed in the case of high conductivity compositions is attributed to the electrode polarization effects. The observed impedance and modulus spectra in correlation with the Arrhenius plots obtained at different frequencies have clearly indicated the frequency dispersion of conduction due to many-body effects and the formation of a large capacitance associated with the electrodes. Thus, the present analysis has suggested a non-Debye type of relaxation process arising due to many-body effects and a distribution of relaxation times, which is a temperature-independent phenomenon exhibited by the heterogeneous electrical structure of the mixed system.

1. Introduction

Recently, a number of attempts have been made to investigate the behaviour of frequency-dependent conduction (or a.c. conductivity) of fast ionic solids using impedance analysis [1]. In particular, the analysis of a.c. response using both complex impedance and complex electric modulus formalisms has been found to be very useful in the evaluation of d.c. conductivity, conductivity relaxations (bulk and interface), grain-boundary effect, etc. [2]. This is due to the fact that fast ionic conductors are mostly investigated in the form of polycrystalline samples, in which the grain-boundary impedance would influence the analysis of the bulk conductivity values. In the present study, a detailed impedance analysis of the mixed system $(CuI)_{100-x}$–$(Ag_2SO_4)_x$ ($0 \leqslant x \leqslant 60$) over a wide temperature range (293–403 K) has been investigated.

2. Experimental procedure

Powder specimens of different compositions of the mixed system $(CuI)_{100-x}$–$(Ag_2SO_4)_x$ ($0 \leqslant x \leqslant 60$) were prepared as described previously [3] and pressed with reversible (non-blocking) electrodes (i.e. silver powder + specimen in the weight ratio 2:1) on either face under a pelletizing pressure of 4000 kg cm^{-2} (392 MPa) in order to form circular pellets for the frequency response analysis. A Solartron model 1254 FRA system and a Solartron model 1286 electrochemical interface, incorporated with a BBC B + microcomputer in the frequency range 1 Hz–65.5 kHz, and over the temperature range 293–403 K, were used in the present investigation. A chromel–alumel thermocouple was used to record the sample temperature during measurements.

3. Results and discussion

3.1. Impedance spectroscopy

Fig. 1a–c show the conductivity plots (log $\sigma(\omega)$ versus log ω) as a function of temperature for three different compositions having 5, 45 and 60 mol% Ag_2SO_4, respectively, in the mixed system CuI–Ag_2SO_4. From Fig. 1a, it is clear that the conductivity plots for the compositions having very low silver oxysalt (5 mol% Ag_2SO_4) content consist of two distinct regions, an almost frequency-independent plateau region in the low intermediate frequency range and a high-frequency region especially at low temperatures, where $\sigma(\omega)$ varies significantly with frequency, indicating a high-frequency dispersion. As the temperature is increased, the high-frequency dispersion is found to shift towards higher frequencies so that the frequency-independent plateau region alone could be observed.

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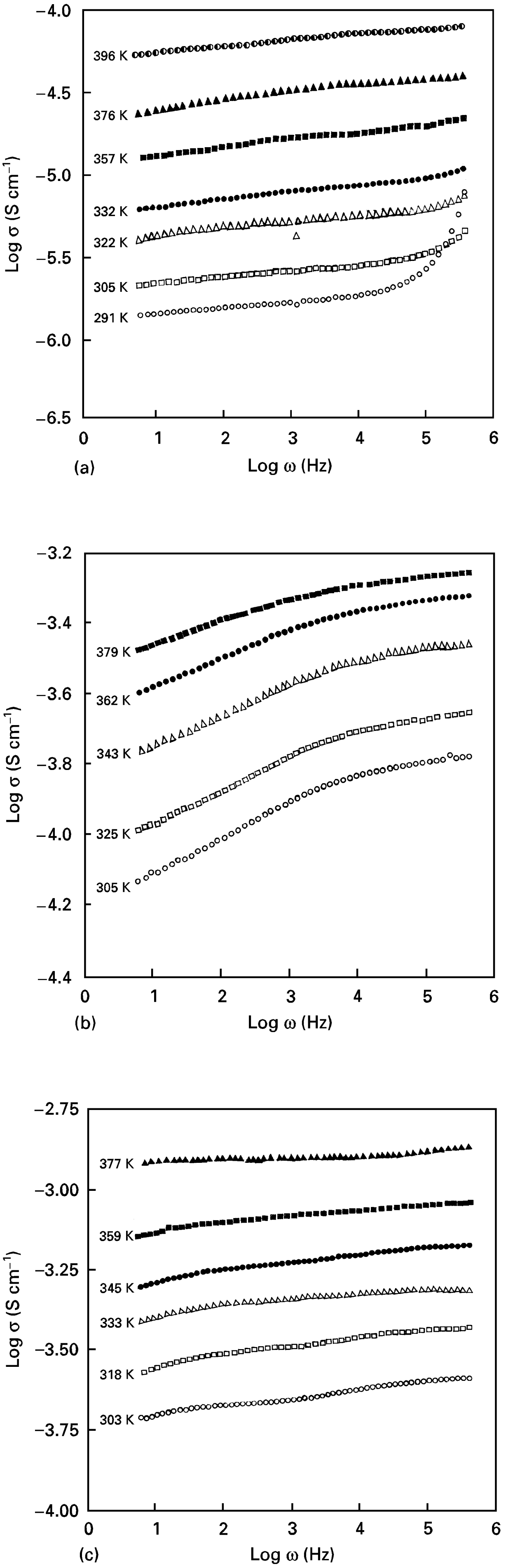

Figure 1 (a) Conductivity plots for the compositions having (a) 5 mol% Ag_2SO_4, (b) 45 mol% Ag_2SO_4, and 60 mol% Ag_2SO_4, in the mixed system $CuI–Ag_2SO_4$.

In Fig. 1b, a low-frequency dispersion region together with a frequency-independent plateau in the intermediate frequency region is present. At higher temperatures, the observed low-frequency dispersion is found to disappear, resulting only in the presence of the frequency-independent region. This type of frequency-dependent behaviour (non-Debye type) of conductivity has also been observed in many fast ionic conductors [4]. These features, which cannot be expressed by a single relaxation equation, can be explained on the basis of Jonscher's universal power law [5]

$$\sigma_{\mathrm{a.c.}}(\omega) = \sigma_0 + A\omega^n \qquad (1)$$

where $\sigma_{\mathrm{a.c.}}(\omega)$ is the conductivity at frequency ω, σ_0 is the limiting zero frequency value of $\sigma_{\mathrm{a.c.}}(\omega)$ which is identified as the d.c. conductivity, $\sigma_{\mathrm{d.c.}}$ and A and n are fitting parameters, (n is the frequency exponent which is temperature-dependent and takes values between 0 and 1, and A is a frequency-independent and temperature-dependent parameter). In particular, this power-law variation at higher frequencies has been extensively studied [6–8]. Accordingly, the high-frequency dispersion present in certain compositions of the present system (low mole per cent Ag_2SO_4) has been attributed to many-body effects arising due to ion–ion interactions within these multiphase systems. On the other hand, the observed strong dispersion in the low-frequency region in Fig. 1b for the high-conductivity compositions (i.e. 45 mol% Ag_2SO_4) may be attributed to the "electrode polarization effect" accompanied by a rapid decrease in conductivity with decreasing frequency, which is otherwise known as "creeping d.c. conductivity" [9].

Table I gives the values of A and n for the typical composition 55 mol% CuI–45 mol% Ag_2SO_4 at different temperatures. It is clear that both A and n are temperature-dependent. In all the specimens, as the temperature is increased, n is found to decrease while A increases with increasing temperature. A similar trend has also been observed by many workers on a number of fast ionic conductors [10, 11]. In the present study, the values of n are found to be quite small compared to those reported for other fast ionic conductors [11]. A comparison of the Anderson–Stuart model [12] with the present data suggests that the mechanism of fast ionic conduction within these materials may be due to the presence of well-defined "pathways" for ionic conduction. The limiting zero frequency values of σ_0, which is identified as $\sigma_{\mathrm{d.c.}}$, have been evaluated at different temperatures by

TABLE I Fitting parameters A and n of Jonscher's universal power law for the composition having 45 mol % Ag_2SO_4 in the $CuI–Ag_2SO_4$ system

	Temperature (K)	n	A (10^{-5} S cm^{-1} rad)
1	305	0.20	7.60
2	325	0.17	10.02
3	343	0.13	17.01
4	362	0.10	26.04
5	380	0.08	34.08

TABLE II Comparison of the $\sigma_{d.c.}$ evaluated from the impedance plots with the σ_0 values determined from the frequency-dependent conductivity spectra for the sample with 45 mol % Ag_2SO_4 in the CuI–Ag_2SO_4 system

	Temperature (K)	$\sigma_{d.c.}$ obtained from impedance plots (10^{-4} S cm^{-1})	σ_0 evaluated from conductivity spectra (10^{-4} S cm^{-1})
1	305	1.64	1.61
2	325	2.74	2.74
3	343	4.33	4.32
4	362	5.96	5.90
5	380	7.15	7.02

extrapolating the intermediate frequency-independent plateau region of the conductivity plots towards the zero frequency. Table II presents the values thus evaluated in the present investigation together with the values of $\sigma_{d.c.}$ obtained from the complex impedance plots for the typical composition 55 mol% CuI–45 mol% Ag_2SO_4. It is clear from Table II that the values of σ_0 and $\sigma_{d.c.}$ are in good agreement with each other, thus emphasizing the precise evaluation of $\sigma_{d.c.}$ from impedance analysis.

Fig. 2 shows the variation of frequency-dependent conductivity, $\sigma(\omega)$, with the inverse of the absolute temperature for a typical composition containing 40 mol% Ag_2SO_4 in the mixed system CuI–Ag_2SO_4. In Fig. 2, it is observed that the linearity of the plots corresponding to different frequencies is slightly distorted at low temperatures. The observed distortion at low temperatures in the high-frequency region indicates the multiple activation energies arising probably due to many-body effects in the case of the present multiphase system. Similar observations have also been made earlier in many solid electrolyte systems [13].

In the present investigation of the CuI–Ag_2SO_4 mixed system, all the experimentally observed features have clearly indicated the non-Debye-like behaviour of their relaxation properties, which can be explained by assuming a distribution of relaxation times (DRT). For a real solid electrolyte system, as in the case of the present system, the equivalent circuit which simulates the electrical response of the system is represented by a series array of RC elements in order to account for its heterogeneous electrical structure resulting from various intragranular regions within the system. Accordingly, a DRT has been considered for the present system as in the case of the other, systems [14]. This is in view of the fact that this system contains two or more phases, thus providing a heterogeneous electrical structure for the individual composition of the multiphase system CuI–Ag_2SO_4 [3].

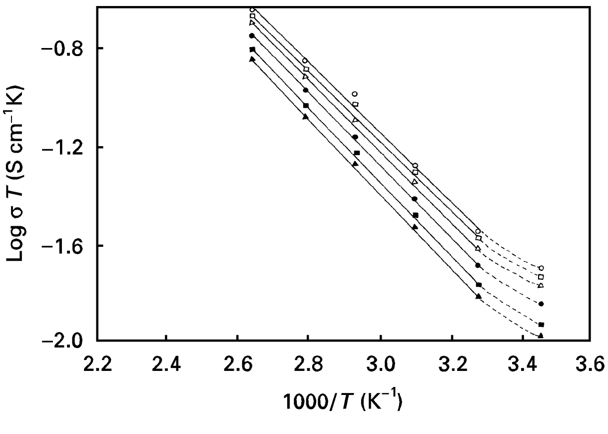

Figure 2 Arrhenius plots of the frequency-dependent conductivity at various frequencies for the composition containing 40 mol% Ag_2SO_4 in the mixed system CuI–Ag_2SO_4. (○) 65.5 kHz, (□) 8.9 kHz, (△) 969 Hz, (●) 105 Hz, (■) 9.2 Hz, (▲) 1.0 Hz.

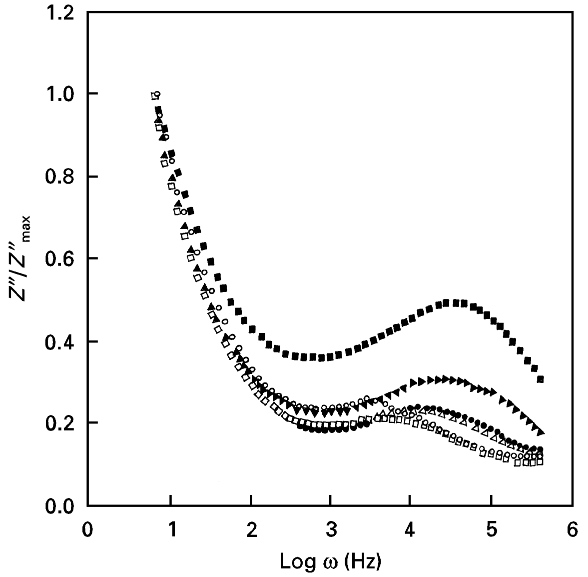

Figure 3 Normalized impedance spectra at different temperatures for the composition containing 40 mol% Ag_2SO_4 in the mixed system CuI–Ag_2SO_4. (○) 303 K, (□) 318 K, (△) 333 K, (●) 345 K, (■) 359 K, (▲) 377 K.

3.2. Impedance spectral data

Fig. 3 shows the typical normalized spectra ((Z''/Z''_{max}) versus log ω) at different temperatures for the composition, 40 mol% CuI–60 mol% Ag_2SO_4. A long tail extending from the low-frequency region up to the intermediate frequency limit and a peaking curve in the high-frequency region are present in the spectrum. The presence of a long tail may be associated with the electrode/electrolyte interfacial effects, and the peaking curve may be related to the bulk of the material. The observed shift in the high-frequency peak towards higher frequencies with increase in temperature suggests that the bulk relaxation is a function of temperature and would occur at higher frequencies at elevated temperatures. These features have been exhaustively exhibited by all practical solid electrolytes, leading to a conclusion that the compositions having high silver ionic conductivity at room temperature, in the mixed system CuI–Ag_2SO_4 including the typical composition 40 mol% CuI–60 mol% Ag_2SO_4, would form a group of promising solid electrolytes for ambient conditions.

3.3. Modulus spectral data

Fig. 4 depicts the normalized modulus spectra ((M''/M''_{max}) versus log ω) at various temperatures for

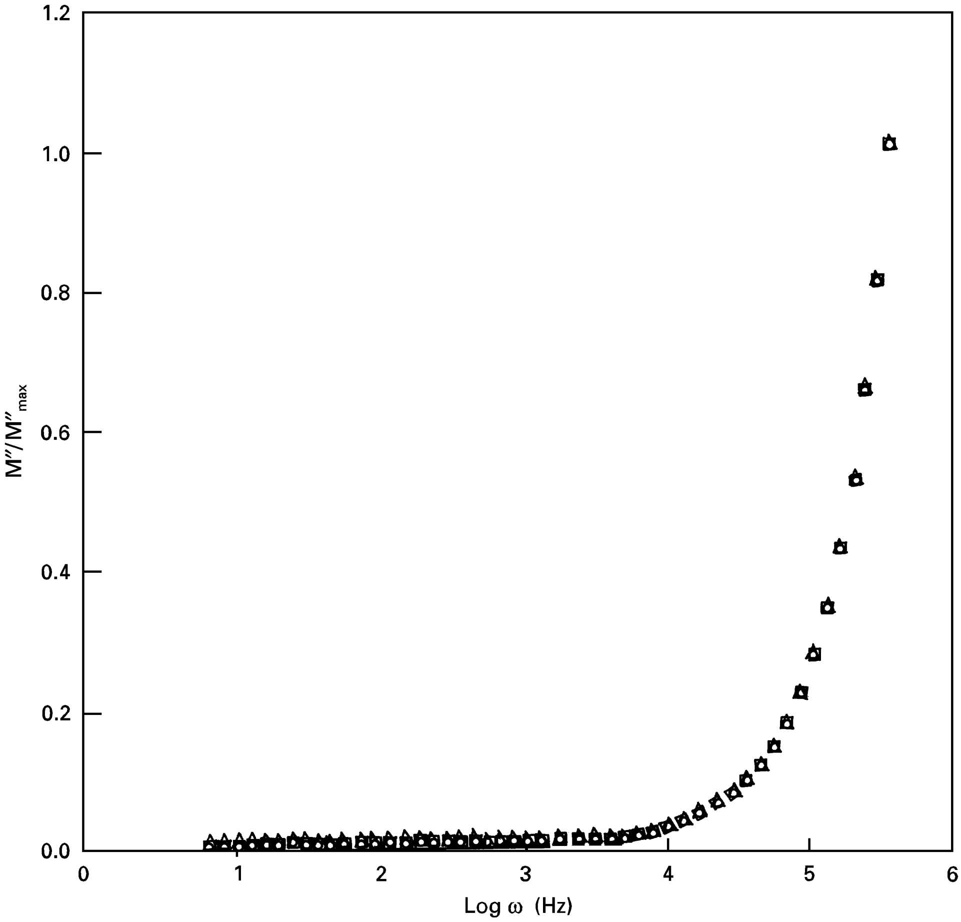

Figure 4 Normalized modulus spectra at different temperatures for the composition containing 45 mol% Ag_2SO_4 in the mixed system CuI–Ag_2SO_4. (□) 303 K, (△) 323 K, (○) 335 K, (■) 348 K, (▲) 371 K, (●) 382 K.

a typical composition containing 45 mol% Ag_2SO_4 in the mixed system CuI–Ag_2SO_4. It is interesting to note that all the plots have a similar shape with a long and flat tail extending from the low-frequency region up to the intermediate frequency region. This type of behaviour may be attributed to the large capacitance associated with the electrodes [2] while that part of the peaking curve observed at higher frequencies may be due to the bulk effect. The non-perturbed shape of the modulus spectra obtained at various temperatures has indicated the temperature independence of the distribution of relaxation times (DRT) because the probability of a single relaxation time is too small, especially when the conductivity is very high, as in the present case [15]. The physical significance of the temperature-independent DRT is that the distribution of conductivities in the specimens due to various layers within the solid, is temperature-independent. It is also clear from these modulus spectra that it is possible effectively to suppress the grain-boundary and electrode effects in the modulus formalism.

4. Conclusion

The frequency-dependent conductivity and modulus spectra of the various compositions of the multiphase system CuI–Ag_2SO_4 have suggested a non-Debye type of relaxation process arising due to many body effects. A distribution of relaxation times (DRT) has been proposed for the conduction mechanism and also for the observed frequency dispersion. It is also concluded that the distribution of relaxation times (DRT) is a temperature-independent phenomenon and that the present system exhibits a heterogeneous electrical structure.

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