Stability Determination of Soy Lecithin-Based Emulsions by Fourier Transform Infrared Spectroscopy

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ABSTRACT: The stability of soy lecithin-stabilized emulsions was determined by Fourier transform infrared spectroscopy. Oil-in-water (o/w) emulsions were prepared with 6% (vol/vol) medium-chain triglycerides (MCT), 94% (vol/vol) water, and 4% (wt/vol) Lecigran and Lecimulthin soy lecithin. There were little or no differences between the 4% Lecigran and 4% Lecimulthin emulsions for all vibrational regions studied (OH at 3348 cm^{-1}, C=O at 1741 cm^{-1}, PO and C–O–C at 1157 cm^{-1}, and P–O–C at 1101 cm^{-1}), but the control emulsion, without emulsifier, had increased vibrations as the emulsion separated. The weaker vibrations of the more stable emulsions were probably due to reduced molecular interaction at the interface. However, added magnesium or calcium chloride enhanced the vibration of these groups, probably by disrupting the lecithin interaction at the emulsion interface.

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KEY WORDS: Fourier transform infrared spectroscopy, Lecigran, Lecimulthin, medium-chain triglyceride, oil-in-water emulsion, phospholipid.

Emulsions are important because they are responsible for controlling physical properties, flavor, and stability in food systems. Various foods are emulsions (butter, milk, ice cream, soups). Oil-in-water (o/w) emulsions are two-phase emulsions in which water is the continuous phase. It is important for an emulsion to maintain its stability in order for it to be a quality product. Emulsions can undergo various changes during storage and handling that may result in partial or complete breakdown and phase separation. It is important to understand the factors contributing to the destabilization of emulsions. A "stable" emulsion is defined as one in which the inevitable process of separation has been slowed to an extent that is not of practical importance during 2 to 3 yr of storage (1). In the emulsification process, energy is required to disperse one liquid into another as droplets. The interfacial area is dramatically increased during this dispersive process. Emulsion instability is complex and includes flocculation, coalescence, creaming, and phase separation. High salt concentrations can affect emulsions by lowering the interfacial tension and breaking the emulsion. Ionic compounds reduce the thickness of the electrical double layer at the oil–water interface, reducing repulsive forces between the droplets and causing coalescence. Emulsion stability is to a large extent determined by interparticle forces, which together with the forces acting between molecules within each aggregate determine the phase behavior of emulsions. The nature of the emulsifier used can add to the shelf life of an emulsion. Lecithin is a natural emulsifier consisting of a mixture of phospholipids (PL), which has been used for centuries in food products (2). The polarity of lecithin makes it a useful emulsifier because it hydrogen bonds to the water and creates a nonpolar interaction with the hydrocarbon chains of medium-chain triglycerides (MCT).

A considerable body of literature exists on the application of Fourier transform infrared spectroscopy (FTIR) to characterize the phase behavior of both naturally occurring and synthetic PL (3), and it has been successfully used to analyze vegetable oil PL (4). FTIR has recently been used by the authors to determine the effect of temperature on the stability of soy-stabilized emulsions (5).

The goal of the present study is to observe the value of FTIR in monitoring emulsion stability and the effect of ionic salts on the stability of these emulsions. FTIR is used to understand the physical and chemical changes in these emulsion systems.

The objectives of this research were (i) to determine the stability of soy lecithin-stabilized emulsions by FTIR by examining changes in PL and MCT interactions; (ii) to determine the effect of two different lecithin emulsifiers by examining changes in the water, PL, and MCT in the emulsion; and (iii) to determine the effect of divalent ions on the stability of these emulsions by FTIR.

MATERIALS AND METHODS

Materials. MCT (Abitec Corporation, Janesville, WI), Lecigran 5750 (Riceland, Stuttgart, AR), Lecimulthin 100 (Lucas Meyer, Decatur, IL), anhydrous magnesium chloride and calcium chloride (Fisher Scientific, Pittsburgh, PA) were used in this study.

Stability of soy lecithin emulsions. O/w emulsions were prepared from 6% (vol/vol) MCT, 94% (vol/vol) water, and 4% (wt/vol) soy lecithin concentrations with either Lecigran 5750 or Lecimulthin 100 commercial emulsifiers. A control was prepared with MCT and water, with no soy lecithin added.

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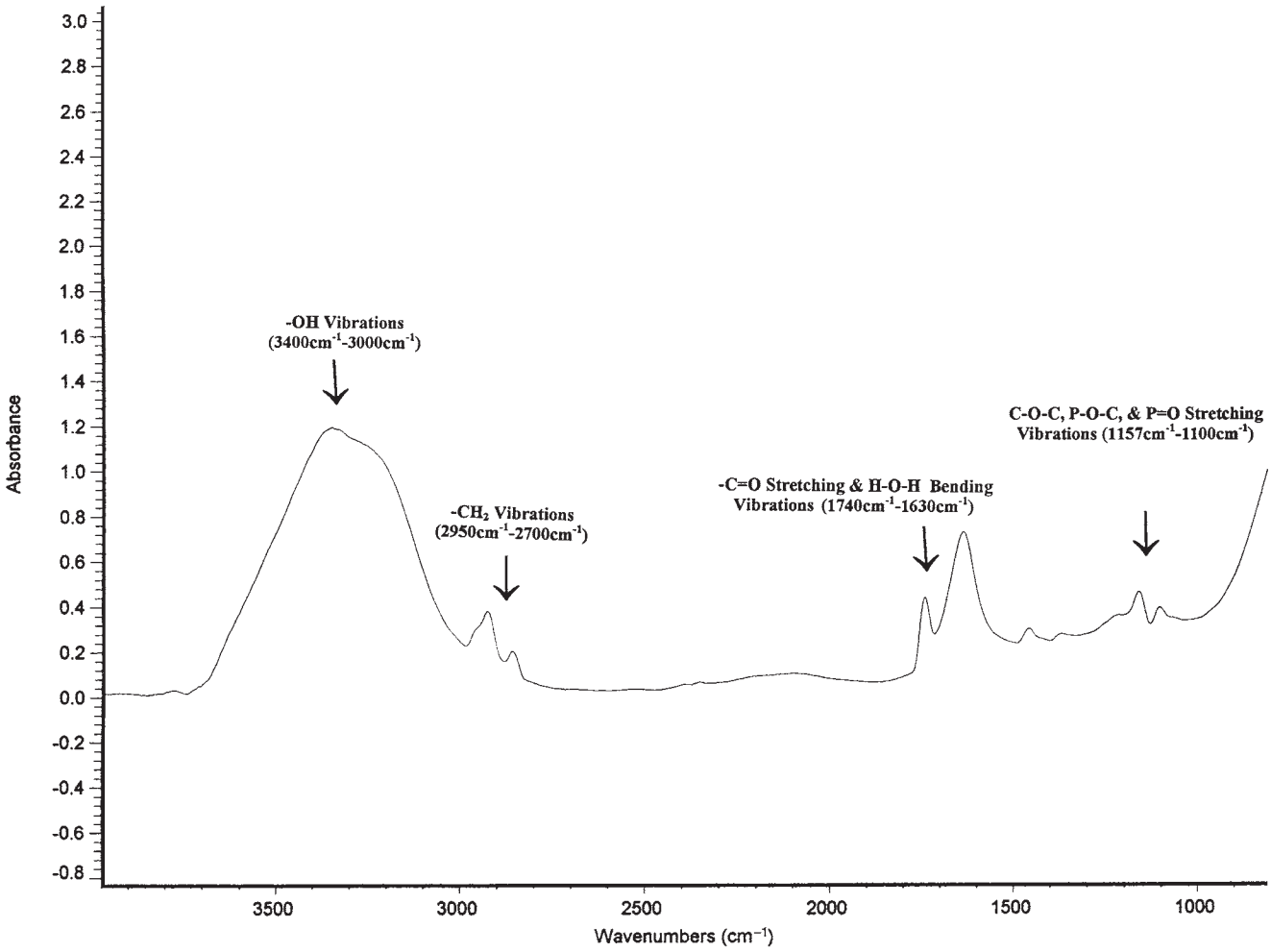

FIG. 1. The Fourier transform infrared (FTIR) spectrum of 4% soy lecithin-stabilized emulsion. One hundred scans were co-added at a resolution of 4 cm^{-1}.

The oil phase containing the MCT and the lecithin was heated to 70°C with stirring. Distilled water and the oil phase were introduced into the reservoir of a two-stage lab homogenizer (model 15 M; Gaulin Corporation, Wilmington, MA) at 3,000 psig pressure and 70°C. To prevent separation of the water and oil phases in the reservoir, a whisk was used to mix the two phases together. The product was collected, recycled twice, and then poured into 250-mL amber bottles. The homogenizer was washed with a dilute sodium hydroxide solution, a dilute acidic solution, and then with hot water between sample preparations. Twelve replicate samples were prepared for each lecithin and the control.

FTIR and pH analyses were conducted every week for 2 wk. An Impact 410 instrument (Nicolet, Madison, WI) was used for spectra collection of the emulsions. A horizontal attenuated total reflectance unit (HATR) with a standard germanium plate was used. Approximately 0.75 mL of emulsion sample was introduced onto the germanium plate. Typically, 100 scans of sample and background were separately co-added at a nominal resolution of 4 cm^{-1}. The germanium plate was cleaned with ethanol and distilled water between runs. The FTIR bands peaks at 3348; 1741; 1157; and 1101 cm^{-1} were used in the determination of emulsion stability. One hundred scans were co-added at a resolution of 4 cm^{-1}.

Effect of divalent salts. Magnesium chloride and calcium chloride were added to determine the effect of salts on emulsion stability and FTIR response. Approximately 50 µL of 0.1, 0.5, 1.0, 3.0, 5.0, and 10.0 mg/mL of magnesium chloride and calcium chloride were added to 100 mL of emulsions stabilized with 4% emulsifiers (Lecigran and Lecimulthin) and the control, to provide approximate salt concentrations of 0.5, 2.5, 5.0, 15, 25, and 50 ppm, respectively. FTIR analysis, as previously described, and pH measurements were made on the emulsions 1 and 2 wk after the addition of the ionic constituents.

Statistical analysis. The Jump™ program (SAS Inc., Cary, NC) was used for determination of differences between and within emulsion samples. The coefficients of variation were determined for data.

RESULTS AND DISCUSSION

Figure 1 shows the regions of the FTIR used to study the stability of the emulsions prepared with 4% lecithin. These regions correspond to OH stretching vibrations between

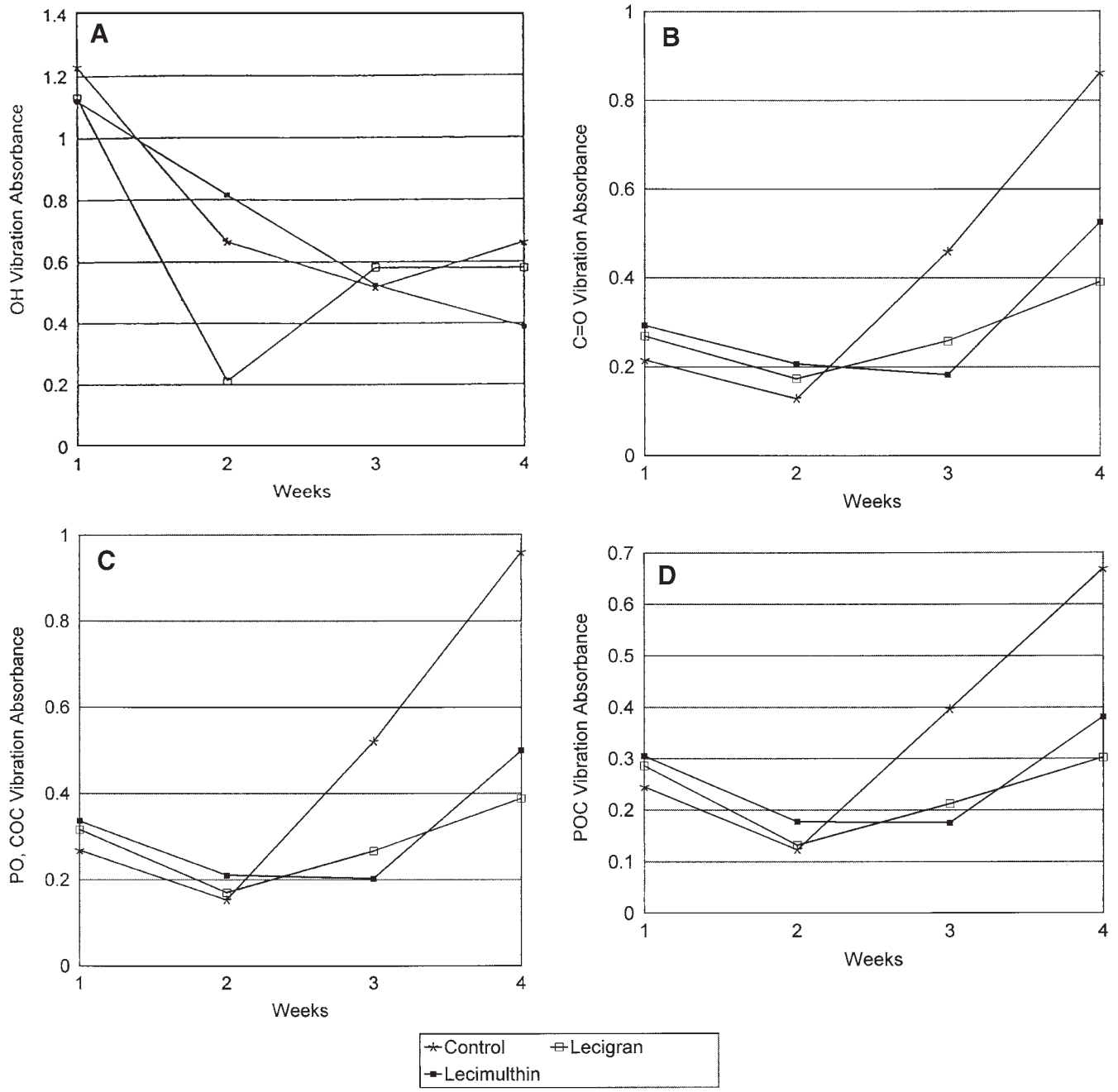

FIG. 2. The average FTIR absorbances of 4% Lecigran, 4% Lecimulthin, and control emulsions for the major vibration peaks from week 1 through week 4. (A) OH peak at 3348 cm^{-1}; (B) C=O peak at 1741 cm^{-1}; (C) PO and C–O–C peaks at 1157 cm^{-1}; and (D) P–O–C peak at 1101 cm^{-1}. One hundred scans were co-added at a resolution of 4 cm^{-1}. See Figure 1 for abbreviation.

3600–3000 cm^{-1}; $-CH_2$ stretching vibrations between 3000–2800 cm^{-1}; –C=O stretching and OH bending vibrations between 1770–1500 cm^{-1}; and C–O–C, P–O–C and P=O stretching vibration between 1200–1050 cm^{-1}.

Stability of soy lecithin emulsions. Figure 2 shows the average absorbance for 4% Lecigran, 4% Lecimulthin and control emulsions from week 1 through week 4 for the different vibrational regions. During week 1 and week 2, absorbances of the OH vibration (Fig. 2A) were similar for all three emulsions and there were no large variations at any given peak region. This suggests that the OH vibration is not a good indicator of relative emulsion stability. However, after week 2, the control produced the largest variation (Fig. 2B–D) for the absorbance ranges shown, indicating that the emulsion was changing rapidly. This may be because the emulsion had no emulsifier and was more susceptible to rapid separation with time. This was due to oil settling out of the control (high variation) and over subtraction of the water spectrum in the emul-

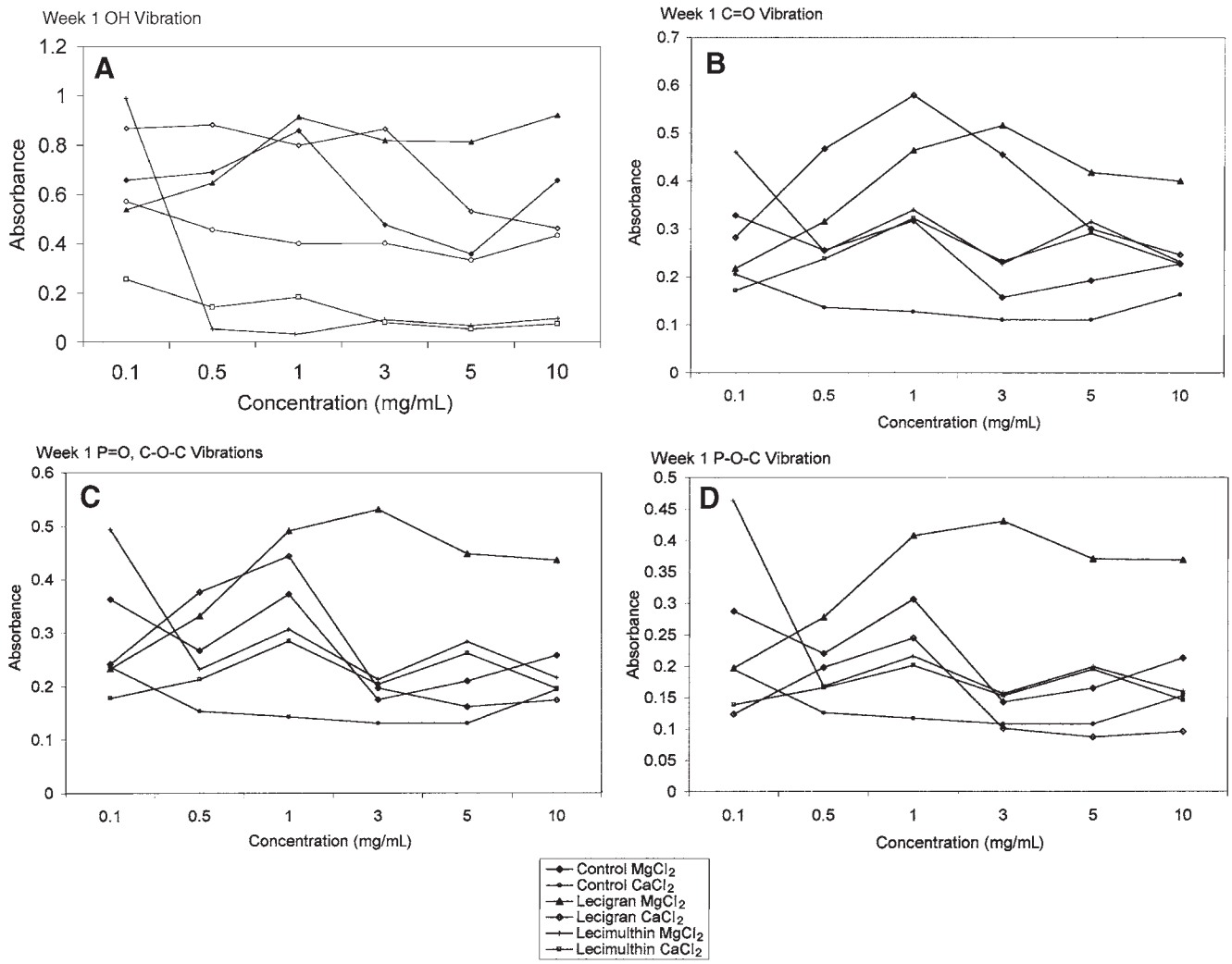

FIG. 3. The effect of addition of $MgCl_2$ and $CaCl_2$ on 4% Lecigran, 4% Lecimulthin, and control emulsions for week 1. (A) OH peak at 3348 cm^{-1}; (B) C=O peak at 1741 cm^{-1}; (C) PO and C–O–C peaks at 1157 cm^{-1}; and (D) P–O–C peak at 1101 cm^{-1}. One hundred scans were co-added at a resolution of 4 cm^{-1}.

sion. The Lecigran and Lecimulthin emulsions gave much lower absorbances than the control from week 1 to week 4, showing that the presence of the emulsifier resulted in much stronger emulsions than the control, which had no emulsifier present. There were little or no differences between the Lecigran and Lecimulthin emulsions for all the vibrational regions studied. Absorbance by the control emulsion, at 1101 cm^{-1}, must be due to a group other than P–O–C, as no lecithin is present. There were no differences in the pH values of Lecigran, Lecimulthin and the control emulsion.

Effect of divalent ions on emulsion stability. Figures 3 and 4 show the effect of addition of calcium chloride and magnesium chloride on emulsion stability for the major peaks for the control and the 4% Lecigran and Lecimulthin emulsions for weeks 1 and 2, respectively. Figure 3A shows the effect of both salts on the OH vibration band at 3348 cm^{-1} at week 1 for the control, Lecigran and Lecimulthin emulsions. The OH vibrations for the 4% Lecigran and the 4% Lecimulthin emulsions were greatly affected by addition of salt. However, the control was not affected as much. Week 2 emulsions (Fig. 4A–D) were all similar except for A, where 4% Lecigran emulsion with added magnesium chloride had much higher absorbances for OH vibration than the rest of the samples. Figure 5 shows the effect of magnesium chloride on the –C=O group vibration of 4% Lecigran emulsion. As concentration of the ionic salt was increased, the vibration of the –C=O group (oil phase) increased. This is probably because the group is released from the interface where it is hydrogen-bonded to water and therefore causes an increased vibration. The absorbance values for all Lecigran and Lecimulthin samples in week 2 were higher than the control. The absorbance difference may be due to salt destabilization of the lecithin–oil interaction at the interface. In week 2, lower concentrations of calcium chloride were found to give the most destabilization while the larger levels of the magnesium chloride gave the most destabilization for the same week.

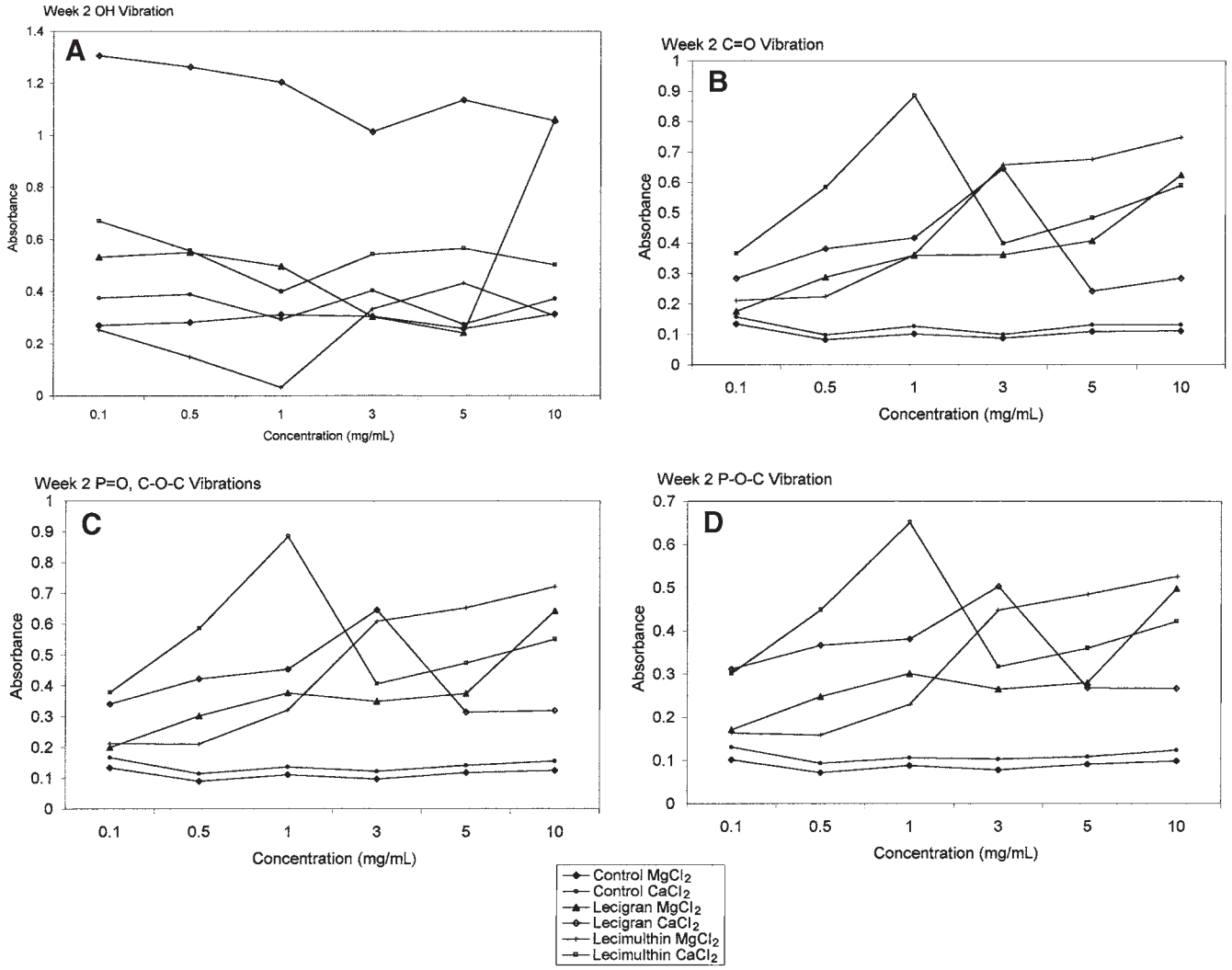

FIG. 4. The effect of addition of $MgCl_2$ and $CaCl_2$ on 4% Lecigran and 4% Lecimulthin and control emulsions for week 2. (A) OH peak at 3348 cm^{-1}; (B) C=O peak at 1741 cm^{-1}; (C) PO and C–O–C peaks at 1157 cm^{-1}; and (D) P–O–C peak at 1101 cm^{-1}. One hundred scans were co-added at a resolution of 4 cm^{-1}.

There were no differences in the pH values of the 4% Lecigran, 4% Lecimulthin and control emulsions on addition of different concentrations of magnesium chloride or calcium chloride (data not presented).

FTIR produced detailed information on the physicochemical characteristics of the soy lecithin-stabilized emulsions, with and without external destabilization. An increase in the absorbance of the individual group vibrations indicated an increase in emulsion destabilization (oil separation), making these groups available for vibration. The control was highly variable because of oil separation and nonuniform sampling, but with emulsifier, the oil remained emulsified and the variability was reduced. Added salts disrupted the emulsion (oil separation), as evidenced by the increased vibration of the individual groups due to oil separating out and being adsorbed onto the germanium surface. No differences in stability were observed between emulsions prepared with Lecigran and Lecimulthin.

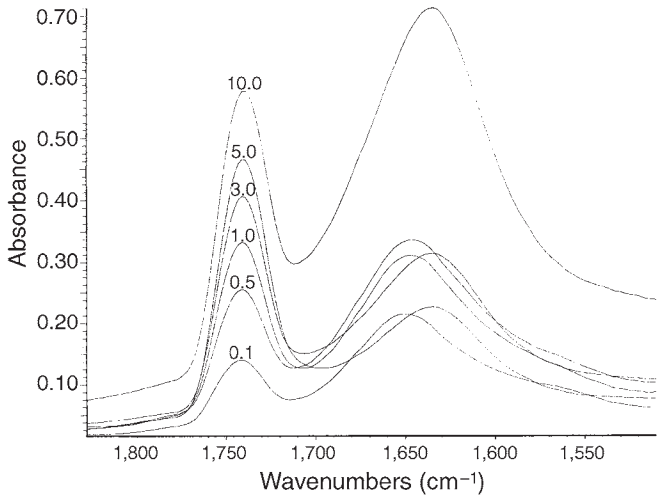

FIG. 5. The FTIR spectra of 4% Lecigran emulsions with 50 µL of 0.1, 0.5, 1.0, 3.0, 5.0, and 10.0 mg/mL of $MgCl_2$ with each 100 mL of emulsion. One hundred scans were co-added at a resolution of 4 cm^{-1}. (*y* axis is not to scale). See Figure 1 for abbreviations.

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