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Qualitative analysis of excess dielectric properties of binary mixtures, ternary mixtures and mixing dynamics measurement using surface plasmon resonance

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Abstract

The analysis of the excess dielectric properties for various binary mixtures and a ternary mixture is demonstrated using a surface plasmon resonance (SPR) sensor. Strong deviations from ideality are seen using SPR to monitor deviations in the dielectric properties following mixing. Binary mixtures with similar refractive index were measured: hexanes/isopropanol, *n*-heptanes/propanol, 1-acetoxy-2-methoxyethane/2-methoxyethanol, butanol/dipropylamine, hexanes/ethylacetate, and ethylacetate/isopropanol binary mixtures. The ternary mixture was composed of 60 different proportions of hexanes, isopropanol, and ethylacetate. Using SPR, mixing dynamics is easily accessible. The mixing of hexanes and isopropanol in static solution was monitored.

Keywords: Fiber-optic; Molecular interactions; Excess properties; Refractive index; Kinetics

1. Introduction

Surface plasmon resonance (SPR) spectroscopy provides an intriguing possibility to rapidly assess the qualitative trends in the thermodynamic mixing properties of binary and ternary solutions. Most SPR studies have involved the analysis of ideal or dilute solutions. However, when concentrated or regular solutions are measured, the behavior of the SPR signal depends strongly on the non-ideality of the solution. Both the SPR signal and the thermodynamics of mixing are related to the dielectric constant of the solution. The SPR signal varies as the dielectric constant and the excess dielectric constant of the mixtures varies. Thus, SPR sensors can be employed to study molecular interactions in many solutions through observing trends in the excess dielectric constant upon mixing.

The excess dielectric constant of mixing for a binary mixture is defined as

$$\varepsilon_{\mathrm{ex}} = \varepsilon_{\mathrm{observed}} - (x_{\mathrm{A}}\varepsilon_{\mathrm{A}}^{0} + x_{\mathrm{B}}\varepsilon_{\mathrm{B}}^{0}) \qquad (1)$$

where $\varepsilon_{\mathrm{ex}}$ is the excess dielectric constant and $\varepsilon_{\mathrm{observed}}$ the actual measured dielectric constant of the mixture. The terms in the parenthesis are the predicted dielectric constant of the mixture based on ideal mixing of mole fractions x_{A} and x_{B} of two pure compounds with dielectric constants $\varepsilon_{\mathrm{A}}^{0}$ and $\varepsilon_{\mathrm{B}}^{0}$. Deviation from ideality is an indication of the molecular interactions. An ideal solution of molecules A and B will have the same interaction between A–A, B–B, and A–B. If the interactions are weaker for A–B than for A–A or B–B, the SPR signal will exhibit a negative excess behavior. If the interactions are stronger between A–B than for A–A or B–B, the SPR signal will exhibit a positive excess behavior. The measurement of this property is important for understanding the solution behavior through the ‘excess properties’ of solutions, that is deviations from ideality.

The use of SPR is increasingly growing. Applications in the fields of biochemistry [1–4], analytical chemistry [5–7],

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physics [8,9], and engineering [10–13] have been previously reported. Calibration of the SPR sensors is done using linear or polynomial models to relate changes in the resonance spectra to constituent concentration [14,15]. SPR has also been used to monitor distillation processes [16]. When the sensor is calibrated in an accessible binding site-limited regime, mostly for biosensors, the SPR signal follows a Langmuir isotherm [17–20]. The excess properties become important when linear calibration is applied. Employing a linear or polynomial calibration model implies that the solution behaves ideally.

SPR has numerous advantages compared to conventional refractive index measurement. SPR sensors can be made smaller using fiber-optic probes than an Abbe refractometer can be. This offers the possibility of remote sensing that is not possible using a standard RI measurement. A typical SPR set-up will offer a greater accuracy than the best Abbe refractometer offered commercially. Normally, refractive index accuracy of 10^{-6} RIU, or better, is reported with SPR while the Abbe refractometer will have at best 10^{-5} RIU.

SPR theory has been extensively described [21,22]. Light undergoing total internal reflection exhibits an evanescent wave. This evanescent wave can excite a standing charge on a thin gold film (Fig. 1). The gold film is typically 50 nm thick. In order for the standing charge excitation on the gold film to occur, it must be in contact with a sample of lower refractive index than the waveguide. Energy transfer occurs when the wavevector of the standing charge k_{sp} and the wavevector of the evanescent wave k_x are equal based on the equations

$$k_{\mathrm{sp}} = k_0\sqrt{\frac{\varepsilon_{\mathrm{m}}\varepsilon_{\mathrm{s}}}{\varepsilon_{\mathrm{m}}+\varepsilon_{\mathrm{s}}}} \tag{2a}$$

$$k_x = k_0\eta_{\mathrm{D}}\sin\Theta_{\mathrm{inc}} \tag{2b}$$

where k_0 is the wavevector of the incident light, ε_{m} and ε_{S} the complex dielectric constants of the metal and the sample, respectively, η_{D} the refractive index of the waveguide and Θ_{inc} the incident angle of the light. Multiple combinations of incident light angles and wavelengths can excite the standing charge. When k_{sp} of Eq. (2a) equals k_x of Eq. (2b) the photon is absorbed, shown by a minimum in the reflection spectra (Fig. 2). Fig. 2 is an experimental spectrum of ethanol referenced to a blank air spectrum. The position of the minimum (λ_{SPR}) is indicative of the dielectric constant, or the refractive index, within 100–200 nm of the gold film. SPR is most sensitive for processes occurring at the surface. The sensitivity decreases exponentially for processes occurring further from the surface.

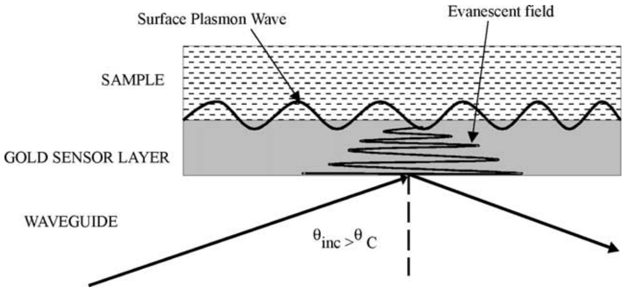

Fig. 1. SPR theory, light excitation of a standing charge on a thin metal film.

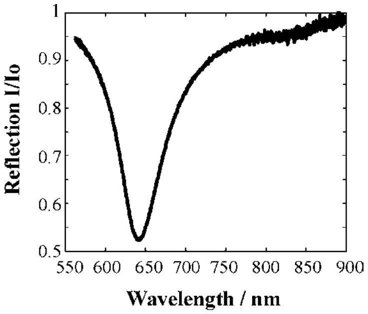

Fig. 2. SPR signal at constant angle.

The excess dielectric constant properties of numerous binary mixtures of organic solvents were measured. Both types of non-ideality, weak and strong interactions, were observed. A ternary excess dielectric diagram was constructed for hexanes, isopropanol, and ethylacetate mixtures. The mixing dynamics for the hexanes and isopropanol system were monitored.

2. Experimental

2.1. SPR sensor system construction

The manufacture of the SPR sensors used in this study has been described previously [14,23,24]. Here 400 μm diameter multimode fiber-optics are employed for the sensor tip. However, multimode fibers as narrow as 50 μm could be used. In the current configuration, fibers 45 mm in length are cleaved. A 11 mm long piece of the buffer protecting the fiber is removed and 5 mm is replaced to protect the mirror on the distal end (Fig. 3). The distal end is polished with 5, 1, and 0.3 μm lapping films. The distal end is then washed with isopropanol and the sensor is dried at 100 °C for 10 min. A 5 nm adhesion

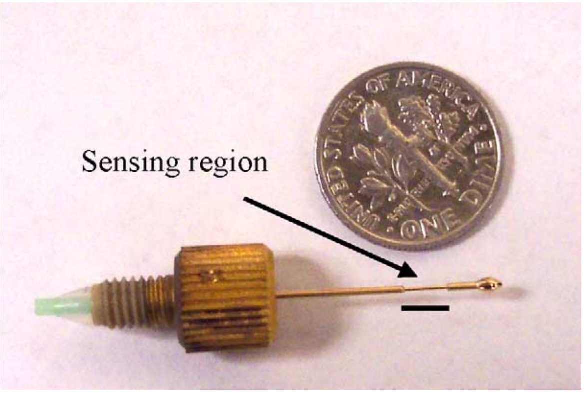

Fig. 3. Optical fiber SPR sensor.

layer of Cr is sputtered on the distal end of the sensor and a 50 nm layer of Au is deposited to form a mirror. The mirror is sealed using oven-cured epoxy. Ten to fifteen millimeters of the buffer on the other end of the fiber is removed. The fiber is installed on the connector and fixed in place using oven-cured epoxy. The connector end is polished using 9, 5 and 1 μm lapping films. The cladding on the sensing area is removed using acetone. The sensor is visually inspected using a microscope objective to ensure that all the cladding has been removed. Five nanometers of Cr and 50 nm of Au are deposited on the sensing area. The sensor is rotated while being sputtered to ensure an even layer of Cr and Au. The probe performance is tested in ethanol. Fig. 3 presents one of the fiber-optic probe tips to scale. Two 200 μm diameter fibers are fitted into the custom design adaptor; one fiber brings light from the white LED employed as a source, the other returns the reflected light to the spectrometer and CCD detector. A Jobin-SPEX 270 M spectrometer with 1800 and 1200 g/mm gratings was used to narrow the spectral range to 42.8 and 71.9 nm, respectively. The spectra were collected with an Andor CCD camera. Resolutions of 0.0421 and 0.0702 nm/pixel are respectively obtained.

2.2. Solution preparation

The chemicals were used without further purification. Hexanes was bought from Mallinckrodt (Phillipsburg, NJ, USA), isopropanol 99.8% was bought from Pharma Product Inc. (Brookfield, CT, USA), and 2-methoxyethanol 99% was bought from Acros Organics (Morris Plains, NJ, USA). *n*-Heptanes 99%, 1-propanol 99%, 1-acetoxy-2-methoxyethane 97%, 1-butanol 99%, dipropylamine 98%, and ethylacetate 99% were bought from Fluka (Milwaukee, WI, USA). The solutions were prepared by weight with measurement accuracy to the nearest 0.1 mg. The total volume of the solutions was 50 mL based on type A volumetric glassware. All solutions were used within 24 h of preparation. The solutions were not degassed but temperature was controlled to 1 °C.

Eleven solutions were prepared for the binary mixtures of hexanes/isopropanol, 1-propanol/*n*-heptanes, 1-acetoxy-2-methoxyethane/2-methoxyethanol, and butanol/dipropylamine. They ranged from a mole fraction of 0–1, covering the entire range of concentrations. The ternary mixtures consisted of 60 solutions of hexanes, isopropanol, and ethylacetate. Three were pure chemicals, 27 were binary mixtures and 30 were ternary mixtures. All mixtures were selected such that the pure components had similar refractive indexes to within 10^{-3} refractive index units.

2.3. SPR measurement

For the binary and ternary samples, the SPR sensor was exposed for about 5 min to the solution in a room temperature water bath. The exposure is for the thermal equilibration of the sample. Then, 100 spectra were acquired and averaged.

For the mixing dynamics, the sensor is equilibrated for approximately 5 min in the first chemical for thermal stability while acquiring the SPR signal. The second chemical is added to the first using a pipette. The only mixing is when the second solution is added. Then the mixture is equilibrated through diffusion of the two chemicals. The SPR signal is acquired throughout the experiment. A SPR spectra is acquired every second, three are added to give one data point.

3. Results and discussion

3.1. Binary mixtures

The systems investigated were selected for the closeness of the refractive index of two or three compounds. Systems with close refractive indices will strongly exhibit the excess properties. These systems also cover the range of polarity. Comparisons between different chemical systems can therefore be more easily made. Because of the limited RI range of the SPR sensors, the systems must also have a refractive index between 1.33 and 1.41. Hexanes and isopropanol were previously investigated for their mixing thermodynamic properties [25,26]. The correlation between the excess properties investigated with the SPR sensors are compared to the excess Gibbs energy in Section 3.4.

3.1.1. Composition effect

The solutions for six different binary mixtures were prepared by weight. The different molar fractions range from pure compound A to pure compound B. The pure component refractive indices are different by almost $\sim 10^{-3}$ RIU for each mixture. This was done to emphasize the non-ideal behavior of the solutions. The mixtures RIs were measured using the SPR sensors (Fig. 4). Using this measurement method, precision of about 5×10^{-6} RIU is achieved. The temperature was controlled to be within 1 °C. A 1 °C temperature change will induce a 0.2 nm SPR shift; given that the SPR shifts observed are much larger than 0.2 nm, it is easily concluded that the observed effect is not temperature induced.

Hexanes and isopropanol have very different polarity. Hexanes are some of the least polar molecules while isopropanol is very polar. These solutions have been previously studied using gas–liquid equilibrium [25,26]. The mixtures exhibited a positive excess Gibbs energy of mixing (Fig. 4A). This can be correlated to the excess SPR measurements. Hexanes and isopropanol mixtures exhibit negative excess SPR. This means that upon mixing, the dielectric constant for the mixture is lower than the ideal one. The dielectric constant ε_r ($\varepsilon_r = \varepsilon/\varepsilon_0$) is therefore closer to the one in vacuum, hence weak interactions between hexanes and isopropanol. ε is the permittivity of the medium and ε_0 is the permittivity of vacuum. This result is in accordance to what was previously found [24,25]. The maximum deviation for the hexanes–isopropanol is at $x_{\text{hexanes}} = 0.50$, where x is the molar fraction. The excess SPR is the deviation from the theoret-

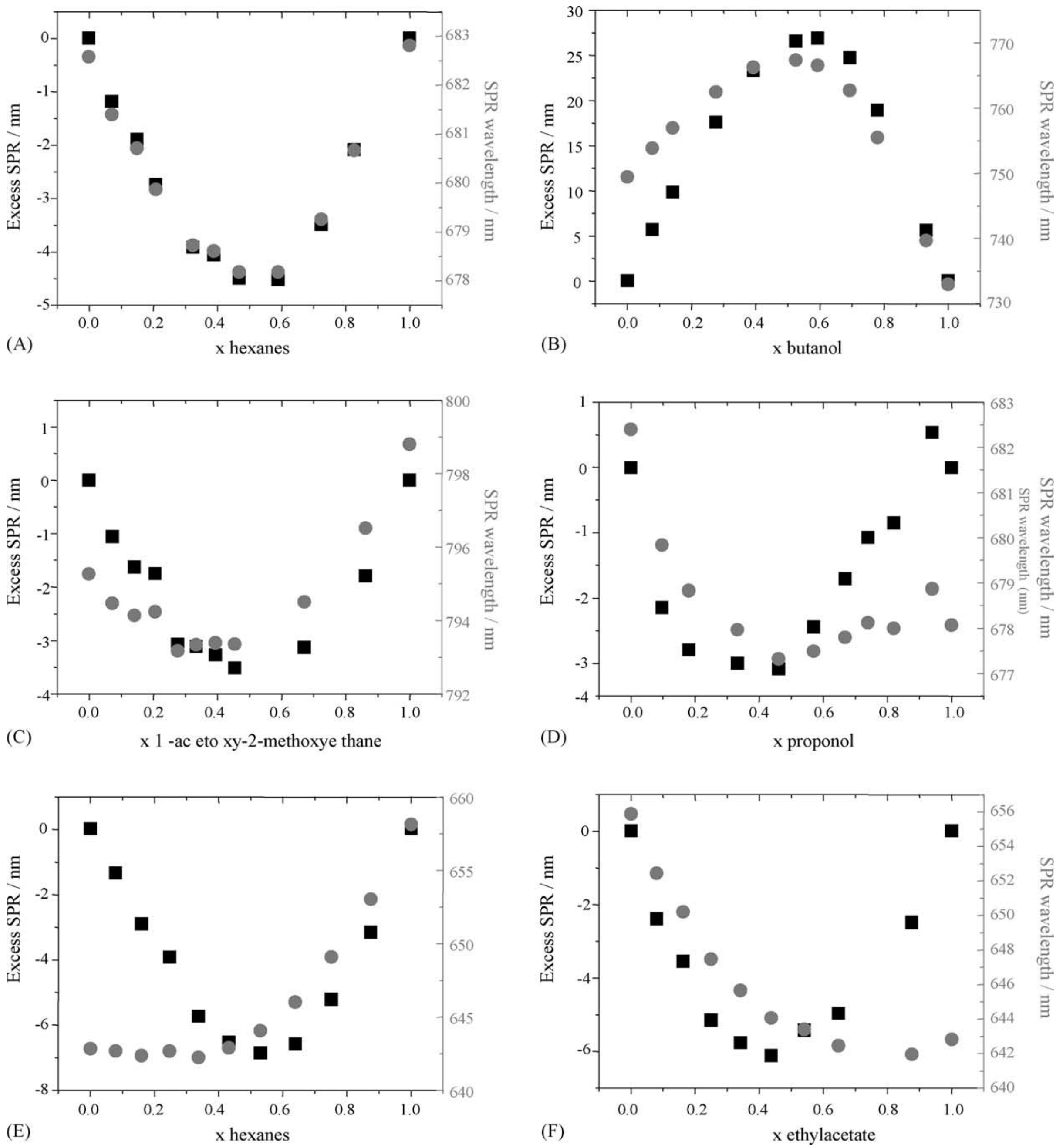

Fig. 4. λ_{SPR} (gray) and excess λ_{SPR} (black) behavior for binary mixtures: (A) hexanes and isopropanol; (B) butanol and dipropylamine; (C) 1-acetoxy-2-methoxyethane and 2-methoxyethanol; (D) propanol and heptane; (E) hexanes and ethylacetate; (F) ethylacetate and isopropanol.

ical linear response of SPR with concentration. The position of the minimum excess SPR shows the contribution of the non-ideality for each component. In this case, both are contributing equally. The minimum excess SPR is at −4.5 nm. The absolute value of excess SPR is a measure of the non-ideality. A greater value indicates a larger deviation from ideality. The excess SPR is matching the non-zero ΔV of mixing (Fig. 5).

Mixtures of butanol and dipropylamine are different from hexanes–isopropanol mixtures by the fact that they are both very polar compounds. The excess SPR shows a positive deviation (Fig. 4B). The positive deviation is characteristic of strongly attractive interactions. Hydrogen bonds can form between these two compounds and cause this attractive force. The absolute value of the excess SPR is a large 27 nm at a molar fraction $x_{\text{butanol}} = 0.55$. This indicates that the attractive forces are very important with butanol contributing slightly more to the non-ideality. These results will be applied to analyze the following mixtures.

A mixture of two structurally similar molecules was analyzed. 1-Acetoxy-2-methoxyethane and 2-methoxyethanol only differ by an acetate group instead of an alcohol.

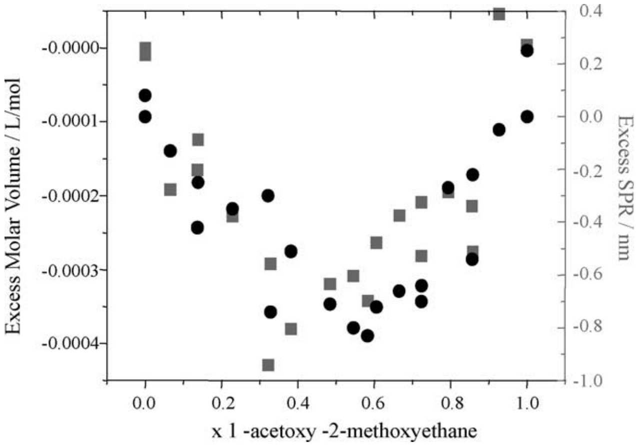

Fig. 5. Comparison of the excess molar volume (black) with the excess SPR (gray) for the mixtures of 2-methoxyethanol and 1-acetoxy-2-methoxyethane. The excess molar volume matches the excess SPR indicating that the deviations from ideality come from the non-zero ΔV of mixing.

The excess SPR signal is negative (Fig. 4C). Therefore the interactions are weak. However, the minimum excess SPR is small at −3 nm. That minimum occurs at $x_{\text{1-acetoxy-2-methoxyethane}} = 0.44$. A small minimum excess value is indicative of a small deviation from ideality; therefore the interactions are only slightly weaker than for an ideal solution. This is in accordance to the fact that the molecules are structurally similar.

Mixtures of propanol and heptanes (Fig. 4D) were prepared to compare to hexanes and isopropanol mixtures. The results are very similar. The excess SPR is also negative, because of the weak interactions between propanol and heptanes. The minimum excess SPR is slightly smaller for the propanol and heptanes mixtures at −3 nm. The maximum deviation from ideality is at the composition $x_{\text{heptanes}} = 0.67$.

Mixtures of hexanes and ethylacetate were measured (Fig. 4E). The interactions are also weak with a negative excess SPR deviation. The minimum SPR is larger than the previous hexanes mixtures at −7 nm. The maximum deviation from ideality is at the composition $x_{\text{hexanes}} = 0.54$ mole fraction.

The last binary mixture is ethylacetate and isopropanol. This can be compared to the 1-acetoxy-2-methoxyethane and 2-methoxyethanol mixture. In both cases, it is mixture of an acetate and an alcohol. Ethylacetate and isopropanol exhibit negative excess SPR (Fig. 4F) as 1-acetoxy-2-methoxyethane and 2-methoxyethanol showed. The minimum excess SPR is larger for ethylacetate and isopropanol mixture at −6 nm. This can be explained by the structurally different ethylacetate and isopropanol. 1-Acetoxy-2-methoxyethane and 2-methoxyethanol have a similar structure. The maximum deviation from ideality is at the composition $x_{\text{ethylacetate}} = 0.43$ mole fraction.

3.1.2. Temperature effect

The SPR signal was collected at 25 and 0 °C for the butanol and dipropylamine mixtures. The solutions were analyzed at room temperature and in an ice bath at 0 °C. The maximum deviation from ideality is of the same magnitude at both temperatures, but a shift of the location where the maximum deviation occurs is observed (Fig. 6). The difference is small. The maximum is at $x_{\text{butanol}} = 0.55$ for 25 °C while it is at $x_{\text{butanol}} = 0.60$ for 0 °C. This means that the dipropylamine's contribution to the non-ideality is more important at lower temperature than room temperature.

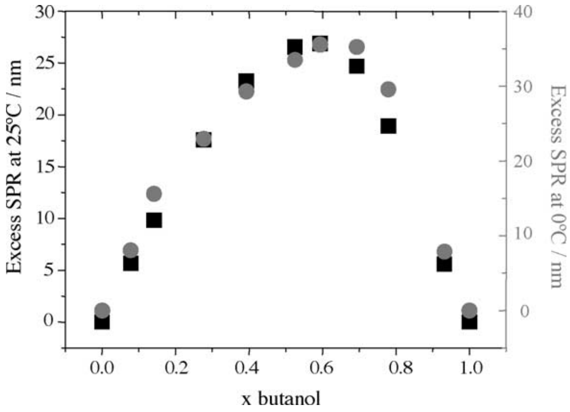

Fig. 6. Temperature effect on the excess SPR for butanol and dipropylamine mixtures: 25 °C (black) and 0 °C (gray).

3.2. Ternary mixture

A ternary mixture of hexanes, ethylacetate and isopropanol was analyzed using SPR. The deviations are negatives, as they were for each binary mixture involving hexanes, isopropanol and/or ethylacetate (Fig. 7). The minimum deviation observed was at $x_{\text{hexanes}} = 0.42$, $x_{\text{ethylacetate}} = 0.44$ and $x_{\text{isopropanol}} = 0.14$. The deviations are a smooth bowl shape from the pure solutions to the minimum excess SPR. The interactions are weak as observed with the binary mixtures of hexanes–isopropanol, hexanes–ethylacetate and ethylacetate–isopropanol. An interesting observation is that with a third compound in the mixtures, the deviations from ideality are greater. With the binary mixtures involving these

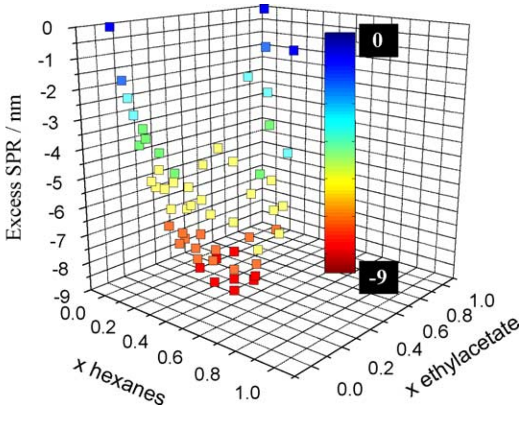

Fig. 7. Excess SPR for ternary mixtures of hexanes, ethylacetate and isopropanol.

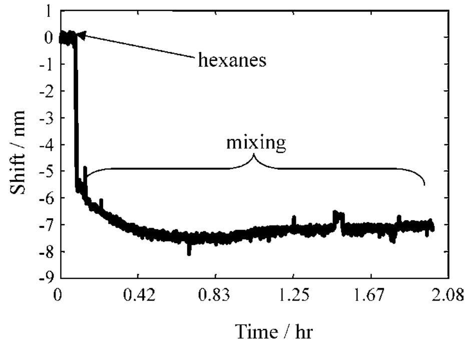

Fig. 8. Mixing of hexanes and isopropanol.

compounds, the maximum absolute deviation was −7 nm for $x_{\text{hexanes}} = 0.54$ and $x_{\text{ethylacetate}} = 0.46$. With the ternary mixture, the maximum absolute deviation is −9 nm. This maximum deviation for the ternary mixture is at a high molar fraction of hexanes and ethylacetate in accordance to what was seen with the binary mixture.

3.3. Mixing dynamics

One of the major advantages of SPR is the ease of monitoring kinetic processes. The mixing of hexanes and isopropanol was measured in real time. The sensor was immerged in 10 mL of hexanes, equilibrated for 5 min and an equal volume of isopropanol was added to the solution (Fig. 8). The equilibrium mole fraction would therefore be 0.370 hexanes. The only mixing in the solution was diffusion of the isopropanol following addition, thus the mixture was equilibrated through a diffusion process. The diffusion of isopropanol into the hexanes can be viewed in Fig. 8. The SPR shift achieves a minimum when the mole fraction at the sensor is $x_{\text{hexanes}} = 0.370$. As the solution near the sensor approaches $x_{\text{hexanes}} = 0.370$, the SPR shift begins to increase. Scaling the initial and minimum shifts to be at $x_{\text{hexanes}} = 1.00$ and $x_{\text{hexanes}} = 0.50$, respectively, Fig. 8 can be related to Fig. 4A as a calibration set to calculate the mole fraction of hexanes at equilibrium. Here the equilibrium concentration is estimated at $x_{\text{hexanes}} = 0.376$. This six parts per thousand error in the mole fraction is reasonable for the calibration model given the minimal controls on constructing the calibration and mixing experiments.

Although the mixing properties can be influenced by a surface, this should not influence the SPR measurement of the mixing dynamics of hexanes and isopropanol. The electrostatic interactions and the electric double layer are short range for organic compounds compared to the SPR sensing depth. The SPR sensing depth is approximately 200 nm while the electrostatic interaction and the electric double layer are in the order of a few nanometers (1–2 nm). The mixtures used in this experiment did not have any particular affinity for gold. For example, if a compound containing a thiol was contacted with the gold surface, then the surface would influence the mixing dynamics because of the reaction of the thiol with the gold surface. Electrolyte solutions mixing would be influenced by the surface to a distance large enough to influence the SPR signal because the electric double layer can extend as far as a few 10s of nanometers.

3.4. Gibbs excess energy correlation to the SPR properties

Fig. 9A shows the SPR signal for hexanes and isopropanol and Fig. 9B shows the excess SPR signal (SPR^{XS}) for the same system. The real signal (black) is the observed experimental SPR shift, and the ideal signal (gray) is based on the linear mixing model for an ideal solution. However, the observed signal is not linear, showing a strong deviation from ideality. The deviation is similar in form to the Gibbs excess energy (Fig. 10). The excess SPR signal can be modeled based on the molar fraction (x) for isopropanol (i) and hexanes (h)

$$SPR^{XS} = SPR - x_{\text{i}}SPR_{\text{i}} - x_{\text{h}}SPR_{\text{h}} \qquad (3)$$

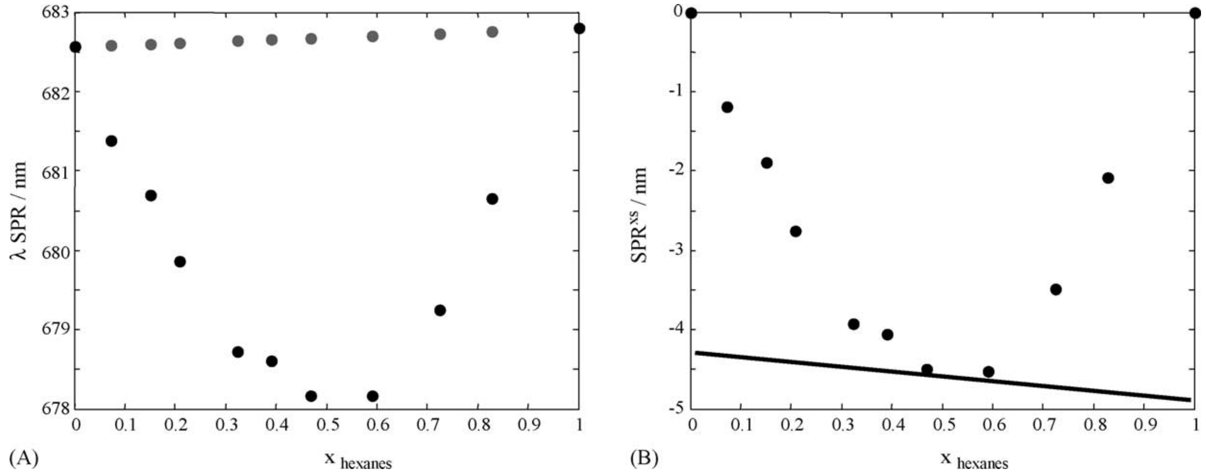

Fig. 9. (A) Measured SPR signal for hexanes–isopropanol at 25 °C (A, black) and the calculated ideal SPR signal (A, gray). Strong deviations are noted for the measured SPR signal compared to the ideal SPR signal; (B) shows the excess SPR. The black line is the tangent of the excess SPR used to calculate the excess SPR for each compounds, hexanes is extrapolated at $x = 1$ and isopropanol is extrapolated at $x = 0$.

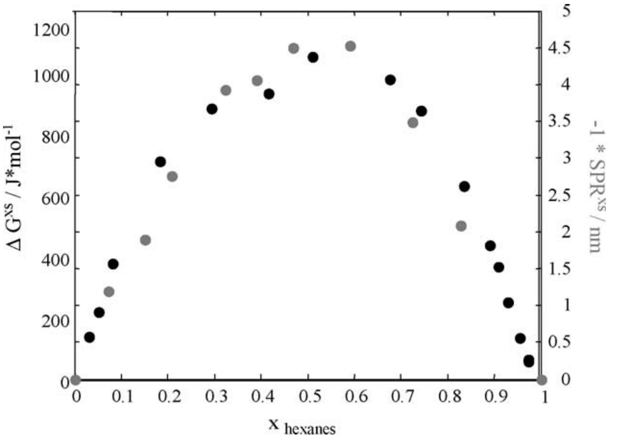

Fig. 10. Comparison of the excess SPR signal (gray) with the Gibbs excess energy of mixing (black). The SPR^{XS} was multiplied by −1 for comparison purposes only.

The SPR^{XS} can be related to the activity coefficient by a proportionality constant, k determined by the method of tangential intercepts [27]. If a tangent is drawn at a fixed composition, the y intercept from the excess SPR signal should be proportional in some way to the activity coefficient. The y intercept for isopropanol is at $x = 0$ and at $x = 1$ hexanes. The slope of the tangent (m) for any mixture can be calculated by

$$m = \left(\frac{\partial F}{\partial x_{\mathrm{i}}}\right)_{x=x_{\mathrm{i}}} \tag{4}$$

where F is least-squares polynomial curve fit to the excess SPR signal. At each mixture (x_{i}) the tangent is extrapolated to $x = 0$ to derive the contribution to SPR^{XS} for isopropanol and to $x = 1$ to derive the contribution to SPR^{XS} for hexanes. These values are plotted against activity coefficients at equivalent fractional volumes for each component (Fig. 11). The activity coefficients were calculated from the work of Barraza and Edwards [25] and Kozhenkov et al. [26].

Table 1
SPR deviation and activity coefficient proportionality constant for hexanes and isopropanol

$x_{\mathrm{hexanes\ (1)}}$	k_{hexanes}	$k_{\mathrm{isoproponal}}$
0.0000		
0.0717	−0.25	1.07
0.1499	−0.22	5.64
0.2092	−0.20	−0.05
0.3247	−0.22	−0.23
0.3898	−0.21	−0.24
0.4690	−0.24	−0.20
0.5903	−0.36	−0.18
0.7250	−0.79	−0.19
0.8276	4.31	−0.23
1.0000		

Relating the activity coefficients to the contribution to SPR^{XS} by

$$k = \frac{a_{\mathrm{i}} - 1}{\text{SPR deviation}} \tag{5}$$

yields a constant around −0.22 for most of the composition range (Table 1). Here k is the proportionality constant, SPR deviation is the value from Fig. 11 and a_{i} is the activity coefficient. The −1 factor in the numerator adjusts that the activity tends towards 1 and the SPR deviation tends towards 0; by subtracting 1 from the activity, both tend towards 0. The deviations of $k = -0.22$ close to $x = 1$ for both hexanes and isopropanol are explained by the higher relative error on the excess SPR signal at those values. Thus, the analysis of the hexanes and isopropanol system allowed finding a proportionality constant in the SPR behavior for the SPR sensor employed that relates the SPR^{XS} to the activity coefficient. Knowing the deviations from the excess SPR signal allows calculating the activity coefficient for future systems using the SPR sensor.

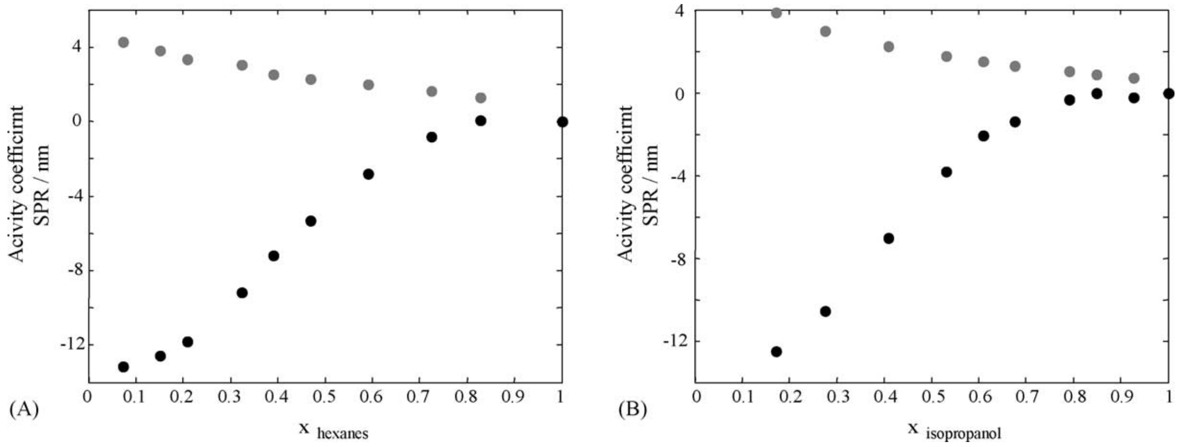

Fig. 11. Activity coefficient and SPR deviation for hexanes (A) and isopropanol (B). The deviations for the SPR signal follow the deviations of the activity coefficient.

4. Conclusions

The measurement of the excess dielectric properties using SPR is reported. Solutions studied demonstrated negative excess SPR, correlated to weak molecular interactions. Only one solution, butanol and dipropylamine, had positive excess SPR characteristics of molecular attraction. This binary mixture also had the largest deviation form ideality with 27 nm excess SPR. SPR at different temperatures was measured for butanol and dipropylamine. The amplitude of the excess SPR is the same at different temperatures, but the position of the maximum excess SPR shifted towards dipropylamine, indicating that dipropylamine has a greater contribution to the non-ideality at lower temperatures. A larger deviation from ideality was observed for a ternary mixture of hexanes, isopropanol and ethylacetate than with the binary mixtures of the same compounds. Adding a third compound increases the non-ideality. Mixing dynamics are accessible using SPR as demonstrated for hexanes and isopropanol. The equilibrium composition corresponds to the solution prepared.

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