| | |
|---|---|
| $\rho$ | density |

*Subscripts*

| | |
|---|---|
| $i$ | component in a mixture |
| m | mixture |
| 1, 2, 3 | component number in a mixture |

**Registry No.** *n*-Hexane, 110-54-3; toluene, 108-88-3; chlorobenzene, 108-90-7; 1-hexanol, 111-27-3.

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# Dielectric Behavior of the Ternary Mixtures of *n*-Hexane, Toluene, Chlorobenzene, and 1-Hexanol

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**Mixture dielectric constants $\epsilon_m$ were measured for the ternaries of *n*-hexane, toluene, chlorobenzene, and 1-hexanol at 30, 40, 50, and 60 °C. Also the values of $\epsilon_m$ were calculated by an equation based on significant liquid structure (SLS) theory using pure-component properties only for the ternaries studied. A comparison of the calculated and experimental data showed that the SLS equation can be safely employed to predict the dependence of $\epsilon_m$ on the composition and the temperature of the systems studied when no ternary or binary experimental $\epsilon_m$ data are available.**

## Introduction

In an earlier work (*1*), experimentally determined mixture dielectric constants were reported for the binaries of *n*-hexane with toluene, chlorobenzene, and 1-hexanol in the temperature range 30–60 °C. A comparison of the experimental data with those calculated by using the Frohlich equation (*2*) and an equation (*1*) based on significant liquid structure (*3*) (SLS) theory showed that the latter gave better results. As an extension to these studies, the present paper reports the measured dielectric constants of the ternary liquid mixtures formed by the same pure components at 30, 40, 50, and 60 °C and provides a comparison of the measured data with those calculated by the ternary form of the SLS equation. It may also be pointed out that the SLS equation (*1*) is applicable in the entire composition range of the liquid mixtures (*1*, *3–5*) involving polar or associated components as against certain simpler equations (*6*) which are satisfactory only in the dilute composition range.

## Experimental Section

Liquid samples similar to those employed in our previous studies (*1*, *7*) were purified (*8*) by fractional distillation and drying before use. The density, viscosity, and refractive index of the purified samples as determined at 25 °C in each case and reported in the preceding paper (*7*) were in reasonable agreement with the corresponding values published in the literature (*1*).

**Table I. Experimental Dielectric Constant $\epsilon_m$ for the Ternary System *n*-Hexane (1)–Toluene (2)–Chlorobenzene (3) at Different Temperatures**

| | | $\epsilon_m$ | | | |
|---|---|---|---|---|---|
| $X_1$ | $X_2$ | 30 °C | 40 °C | 50 °C | 60 °C |
| 0.0484 | 0.5975 | 3.235 | 3.214 | 3.183 | 3.130 |
| 0.1144 | 0.4638 | 3.386 | 3.349 | 3.132 | 3.276 |
| 0.1665 | 0.5544 | 2.927 | 2.906 | 2.870 | 2.849 |
| 0.2161 | 0.2050 | 3.823 | 3.782 | 3.724 | 3.678 |
| 0.2862 | 0.0623 | 3.927 | 3.891 | 3.849 | 3.777 |
| 0.3430 | 0.1481 | 3.464 | 3.443 | 3.396 | 3.359 |
| 0.4056 | 0.4351 | 2.463 | 2.448 | 2.432 | 2.406 |
| 0.4827 | 0.2867 | 2.568 | 2.547 | 2.536 | 2.505 |
| 0.5470 | 0.3824 | 2.145 | 2.135 | 2.125 | 2.109 |

### Experimental Measurements

Ternary mixtures were prepared by weighing the desired pure components with an accuracy of 0.0001 g in a chemical balance using certified weights. The procedure remained the same as that followed in the case of binary mixtures (*1*, *9*), and, knowing the component weights, we calculated the exact compositions. Mixture dielectric constants of the same stock solution (*7*) were measured at 30, 40, 50, and 60 °C as described elsewhere (*1*) by using a Toshniwal dipolemeter type RL 09 working on the heterodyne beat principle. In each case, the cell temperature was maintained by circulating thermostated water from a temperature bath whose temperature was monitored to 0.01 °C with a standardized Beckmann thermometer. The accuracy of measured mixture dielectric constants was found to be within 2% at 30, 40, and 50 °C whereas it was considered within 3% for the measurements at 60 °C. The molar volumes (*1*) as calculated from the measured densities were considered significant to four figures (*1*) whereas required refractive indices were obtained at desired temperatures from smoothened literature data significant to five figures (*8*, *10*, *11*).

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**Table II. Experimental Dielectric Constant $\epsilon_m$ for the Ternary System *n*-Hexane (1)–Chlorobenzene (2)–1-Hexanol (3) at Different Temperatures**

| | | $\epsilon_m$ | | | |
|---|---|---|---|---|---|
| $X_1$ | $X_2$ | 30 °C | 40 °C | 50 °C | 60 °C |
| 0.0503 | 0.6492 | 5.605 | 5.517 | 5.392 | 5.204 |
| 0.1212 | 0.5138 | 5.501 | 5.392 | 5.241 | 5.058 |
| 0.1709 | 0.5951 | 4.829 | 4.767 | 4.683 | 4.595 |
| 0.2392 | 2.2374 | 5.861 | 5.736 | 5.600 | 5.402 |
| 0.3240 | 0.0737 | 6.528 | 6.361 | 6.121 | 5.866 |
| 0.3755 | 0.1695 | 4.678 | 4.599 | 4.496 | 4.391 |
| 0.4095 | 0.4593 | 3.641 | 3.631 | 3.605 | 3.547 |
| 0.4972 | 0.3088 | 3.360 | 3.339 | 3.287 | 3.245 |
| 0.5446 | 0.3980 | 3.136 | 3.109 | 3.089 | 3.057 |

**Table III. Experimental Dielectric Constant $\epsilon_m$ for the Ternary System *n*-Hexane (1)–Toluene (2)–1-Hexanol (3) at Different Temperatures**

| | | $\epsilon_m$ | | | |
|---|---|---|---|---|---|
| $X_1$ | $X_2$ | 30 °C | 40 °C | 50 °C | 60 °C |
| 0.0518 | 0.6389 | 3.485 | 3.427 | 3.370 | 3.255 |
| 0.1240 | 0.5027 | 3.844 | 3.777 | 3.693 | 3.563 |
| 0.1754 | 0.5843 | 2.979 | 2.938 | 2.922 | 2.849 |
| 0.2417 | 0.2294 | 5.079 | 4.933 | 4.767 | 4.522 |
| 0.3250 | 0.0708 | 5.991 | 5.731 | 5.491 | 5.183 |
| 0.3783 | 0.1634 | 4.147 | 4.053 | 3.954 | 3.829 |
| 0.4178 | 0.4482 | 2.390 | 2.377 | 2.364 | 2.354 |
| 0.5040 | 0.2994 | 2.542 | 2.526 | 2.515 | 2.505 |
| 0.5542 | 0.3874 | 2.119 | 2.109 | 2.099 | 2.088 |

**Table IV. Experimental Dielectric Constant $\epsilon_m$ for the Ternary System Toluene (1)–Chlorobenzene (2)–1-Hexanol (3) at Different Temperatures**

| | | $\epsilon_m$ | | | |
|---|---|---|---|---|---|
| $X_1$ | $X_2$ | 30 °C | 40 °C | 50 °C | 60 °C |
| 0.0614 | 0.6417 | 5.741 | 5.600 | 5.454 | 5.272 |
| 0.1455 | 0.4997 | 5.364 | 5.449 | 5.339 | 5.189 |
| 0.2027 | 0.5723 | 4.975 | 4.876 | 4.772 | 4.636 |
| 0.2795 | 0.2248 | 5.923 | 5.757 | 5.527 | 5.329 |
| 0.3715 | 0.0686 | 6.079 | 5.903 | 5.652 | 5.366 |
| 0.4259 | 0.1559 | 4.928 | 4.819 | 4.694 | 4.537 |
| 0.4610 | 0.4192 | 3.948 | 3.902 | 3.859 | 3.792 |
| 0.5496 | 0.2766 | 3.714 | 3.688 | 3.636 | 3.584 |
| 0.5960 | 0.3531 | 3.469 | 3.427 | 3.386 | 3.344 |

**Table V. Values of Molar Volume, Refractive Index, Adjustable Parameter *G* in the SLS Equation, $V_s$, Dipole Moment, and Molecular Weight for Selected Liquids**

| parameter | $t$, °C | *n*-hexane | toluene | chloro-benzene | 1-hexanol |
|---|---|---|---|---|---|
| $V$, cm$^3$ mol$^{-1}$ | 30 | 130.9 | 106.3 | 102.3 | 125.6 |
| | 40 | 132.2 | 107.8 | 102.9 | 126.1 |
| | 50 | 133.9 | 108.4 | 103.4 | 126.7 |
| | 60 | 135.5 | 108.7 | 103.9 | 127.2 |
| $n_D$[a–c] | 30 | 1.3699 | 1.4918 | 1.5194 | 1.4140 |
| | 40 | 1.3642 | 1.4862 | 1.5143 | 1.4100 |
| | 50 | 1.3589 | 1.4810 | 1.5092 | 1.4059 |
| | 60 | 1.3540 | 1.4760 | 1.5045 | 1.4018 |
| $G$[d] | 30 | 0.9118 | 0.1951 | 0.2770 | 1.356 |
| | 40 | 1.399 | 0.2118 | 0.2863 | 1.283 |
| | 50 | 1.829 | 0.2444 | 0.2952 | 1.242 |
| | 60 | 2.207 | 0.2752 | 0.2997 | 1.211 |
| $V_s$, cm$^3$ mol$^{-1}$ | | 104.3[e] | 89.53[e] | 89.50[e] | 110.4[e] |
| $\mu$, D | | 0.085[a] | 0.31[a] | 1.54[a] | 1.55[a] |
| $M$ | | 86.178[a] | 92.142[a] | 112.56[a] | 102.178[a] |

[a] Reference *8*. [b] Reference *10*. [c] Reference *11*. [d] Reference *1*. [e] Reference *12*.

**Table VI. Root Mean Square Deviations in SLS Equation Used in Prediction of Mixture Dielectric Constants**

| | rmsd[a] | | | | |
|---|---|---|---|---|---|
| system | 30 °C | 40 °C | 50 °C | 60 °C | av |
| *n*-hexane (1)–toluene (2)–chlorobenzene (3) | 0.1145 | 0.1125 | 0.1028 | 0.1044 | 0.1086 |
| *n*-hexane (1)–chlorobenzene (2)–1-hexanol (3) | 0.1582 | 0.0956 | 0.0916 | 0.0913 | 0.1092 |
| *n*-hexane (1)–toluene (2)–1-hexanol (3) | 0.0193 | 0.0272 | 0.0333 | 0.0277 | 0.0269 |
| toluene (1)–chlorobenzene (2)–1-hexanol (3) | 0.1036 | 0.0913 | 0.0850 | 0.0834 | 0.0921 |
| | | | | | 0.0842 (overall av) |

[a] rmsd = $[\sum_{i=1}^{K}\{(\epsilon_{\text{exptl}} - \epsilon_{\text{calcd}})/\epsilon_{\text{exptl}}\}_i^2/K]^{1/2}$ where $K$ is the number of data.

## Results and Discussion

The experimental dielectric constant–composition–temperature data for the title ternary mixtures are presented in Tables I–IV, which exclude the pure-component $\epsilon$–$T$ data as the same have been reported in an earlier communication (*1*). The prediction calculations for ternary dielectric constants were carried out from the following ternary form of the SLS equation (1):

$$\frac{3\epsilon_m(\epsilon_m - n_m^2)}{(2\epsilon_m + n_m^2)} = \frac{4\pi N}{V_m}\left[\frac{\epsilon_m(n_m^2 + 2)}{2\epsilon_m + n_m^2}\right]^2\left[\frac{V_{sm}}{V_m}\left(\frac{X_1^2\mu_1^2G_1}{kT} + \frac{X_2^2\mu_2^2G_2}{kT} + \frac{X_3^2\mu_3^2G_3}{kT} + \frac{2X_1X_2\mu_1\mu_2G_{12}}{kT} + \frac{2X_2X_3\mu_2\mu_3G_{23}}{kT} + \frac{2X_1X_3\mu_1\mu_3G_{13}}{kT}\right) + \frac{V_m - V_{sm}}{V_m}\left(X_1\frac{\mu_1^2}{3kT} + X_2\frac{\mu_2^2}{3kT} + X_3\frac{\mu_3^2}{3kT}\right)\right] \quad (1)$$

where $\epsilon$ is the dielectric constant, $k$ is the Boltzmann constant, $\mu$ is the dipole moment of the free molecule, and $V_s$ is the molar volume of the substance just before melting. The value of $V_s$ was obtained by the method (*12*) described earlier. The values of $n_m$, $V_m$, and $V_{sm}$ can be given in terms of pure-component properties and mole fraction $X$ by using the following appropriate mixing equations (*3*, *13*):

$$V_m = X_1V_1 + X_2V_2 + X_3V_3 \quad (2)$$

$$V_{sm} = X_1V_{s_1} + X_2V_{s_2} + X_3V_{s_3} \quad (3)$$

$$n_m = X_1^2n_1 + X_2^2n_2 + X_3^2n_3 + 2X_1X_2n_{12} + 2X_2X_3n_{23} + 2X_3X_1n_{31} \quad (4)$$

$$n_{ij} = [n_in_j]^{1/2} \qquad G_{ij} = [G_iG_j]^{1/2}$$

The subscript m stands for mixture and $G$ is the correlation parameter. For each pure liquid, the value of $G$ at each temperature was calculated by using an equation obtained by putting $X_2$ and $X_3 = 0$ and dropping the subscript in eq 1. The values of $V$, $V_s$, $n$, $\mu$, and $G$ for the ternary components were taken from an earlier work (*1*) and are listed in Table V.

The experimental $\epsilon_m$–$X$–$T$ data were compared with those predicted by eq 1. The root mean square (rms) deviations, as calculated in each case, are listed in Table VI. For *n*-hexane (1)–toluene (2)–chlorobenzene (3), *n*-hexane (1)–chlorobenzene (2)–1-hexanol (3), *n*-hexane (1)–toluene (2)–1-hexanol (3), and toluene (*1*)–chlorobenzene (*2*)–1-hexanol (3) systems the averages of the rms deviations in the temperature range studied are 0.1086, 0.1092, 0.0269, and 0.0921, respectively, with an overall average of 0.0842 for all the systems taken together. A close look at Table VI reveals that the rms deviations gen-

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erally decrease with the increase in temperature except for the ternary *n*-hexane (1)–toluene (2)–1-hexanol (3), for which the trend is reversed. Further, a comparison of the deviations for the ternaries studied (Table VI) with those of their binary subsystems reported earlier (*1*) shows that in the case of *n*-hexane (1)–chlorobenzene (2)–1-hexanol (3) and toluene (1)–chlorobenzene (2)–1-hexanol (3), systems, the order of the magnitudes of rms deviations is the same as that for their binary subsystems while for the *n*-hexane (1)–toluene (2)–chlorobenzene (3) system the rms deviations are somewhat higher than those obtained for the corresponding binary subsystems. Thus, eq 1 can safely be employed to predict the dependence of ternary dielectric constants on the composition and temperature for the systems studied when no ternary or binary experimental dielectric constant data are readily available.

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### Glossary

| | |
|---|---|
| $k$ | Boltzmann constant |
| $n$ | refractive index |
| $G$ | SLS correlation parameter (eq 1) |
| $M$ | molecular weight |
| $N$ | Avogadro's number |
| $T$ | absolute temperature |
| $V$ | molar volume at the temperature of investigation, $cm^3\ mol^{-1}$ |
| $V_s$ | molar volume of a substance just before melting, $cm^3\ mol^{-1}$ |
| $X_i$ | mole fraction of component $i$ |
| rmsd | room mean square deviation |
| $K$ | number of data |
| *Greek Letters* | |
| $\epsilon$ | dielectric constant |
| $\mu$ | dipole moment of the free molecule, D |
| *Subscripts* | |
| D | for sodium light |
| $i$, $j$ | component in a mixture |
| m | mixture |
| 1, 2, 3 | component numbers in a mixture |

**Registry No.** *n*-Hexane, 110-54-3; toluene, 108-88-3; chlorobenzene, 108-90-7; 1-hexanol, 111-27-3.

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# Densities of Aqueous Solutions of NaCl, $MgCl_2$, KCl, NaBr, LiCl, and $CaCl_2$ from 0.05 to 5.0 mol $kg^{-1}$ and 0.1013 to 40 MPa at 298.15 K

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**The density differences, $\Delta\rho = \rho - \rho_0$ (where $\rho$ = density of the solution and $\rho_0$ is the density of $H_2O$), of NaCl, $MgCl_2$, KCl, NaBr, LiCl, and $CaCl_2$ aqueous solutions have been measured from 0.1013 to 40 MPa and for molalities of 0.05–5.0 mol $kg^{-1}$ at 298.15 K. ($MgCl_2$ and KCl molality ranges were 0.05–3.0 mol $kg^{-1}$.) These results have been least-squares fitted by a polynomial equation in molality and pressure, with standard errors less than 50 × $10^{-6}$ g $cm^{-3}$. A comparison of these equations with available literature data is also included.**

### Introduction

Densities of aqueous electrolyte solutions at room temperature and atmospheric pressure are readily available (*1–8*). Reliable measurements have been made for a variety of systems at elevated pressure (*7–10*). Unfortunately, these measurements have been confined to narrow concentration ranges at low concentration (with the exception of NaCl). Sound velocity measurements have been made on all of these salts at 25 °C and atmospheric pressure (*11*, *12*) (NaCl and $MgCl_2$ sound velocities have been measured as a function of pressure to 1.0 mol $kg^{-1}$) (*13*). The purpose of this research is to obtain density measurements at room temperature and elevated pressures (0.1–40 MPa) over a wide concentration range (0.05–5.0 mol $kg^{-1}$). These data are required for calculations involved with mass flow calorimeters and high-temperature mercury displacement type densimeters (*14–16*). The results presented in this paper were measured on a vibrating tube type densimeter. Empirical fits of these measurements are also included.

### Experimental Section

The vibrating tube densimeter, designed and built by H. J. Albert, has been described in detail elsewhere (*18*). The addition of a NESLAB Endocal refrigerated circulating bath to cool the outer jacket of the densimeter was the only modification required to run this instrument at 298 K. The instrument was calibrated, as is necessary for all vibrating tube type densimeters, by using water (*19*) and nitrogen at experimental pressure

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