Relationship between Refractive Index and Molar Concentration of Multi-Component Solutions

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Abstract. Variations in molar densities and solute properties, which together form a solution's basic index, can cause changes in the solution's refractive index. The linear relationship between the ternary system's refractive index solution and each solute's molar concentration can be determined through ternary system solution analysis on light passing through the solution. Experiments were conducted on a CuSO4-NaCl-H2O solution's refractive index in this study. The model utilized here can be further applied to multi-component solutions, as the solution's refractive index has a linear relationship with the properties of each solute. A new refractive index model can be derived accordingly to further enhance the results.

Introduction

The refractive index is a fundamental property of a solution which can vary with temperature, composition, concentration [1], and incident light wavelength [2]. The relationship between the solution concentration and refractive index has many applications such as measuring sea salt concentration [3] and beer quality assessment [4]. Glover et al. [5] investigated the relationship between sucrose solution concentration, mass concentration, and the refractive index to establish an index characterized by the time it takes a beam of light to pass through a unit volume of a given solution. Zhang et al. [6] proposed a linear correlation to a binary solution's refractive index ($\delta = An + B$) based on Lorentz's electronics theory, Lambert's law, and Beer's law. Zhu et al. [7] experimentally investigated the relationship between a ternary inorganic solution's molar concentration and its refractive index, which is also linear. According to the electron cloud inductor model, Zhang [8]suggested that a solution's refractive index can be expressed as $n = 1 + \sum (\rho_m D_m)_i$.

This study was carried out based on the refractive index correlation of Snell's law. The influence of variations in a molar solution concentration on its refractive index was investigated by analyzing light passing through solutions with different molar concentrations. The multi-component solution refractive index varied linearly with each solute's molar concentration under the interaction conditions between solute ions and various volumes after controlling for dissolution.

The Model of Ternary System Solution

As Snell's law suggests, the refractive index of a medium is the ratio of the incident angle's sine to the refracted angle's sine considering the light incidence from the vacuum into the medium, i.e.:

$$n = \frac{c}{v} = \frac{\sin \theta_1}{\sin \theta_2} \tag{1}$$

Where c is the speed of light in a vacuum, v is the speed of light in the medium, and θ_1 and θ_2 are the incident and refracted angles, respectively.
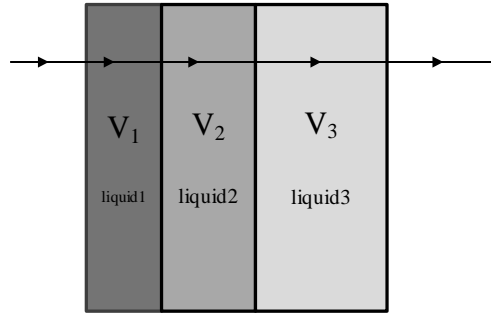
Fig. 1 Schematic diagram of light path through ternary system solution

As shown in Fig. 1, the solution volume is weak because the solid solute dissolves in a solvent. The ternary system solution (two solutes dissolved in a solvent) can also be regarded as a triple-liquid combination with constant molar concentration and refractive index. Liquids 1 and 2 are solutions with constant molar concentration and refractive index which combine withsolutesX_1 andX_2, respectively. Liquids 1 and 2 molar concentrations are *kmol/L* and liquid 3 is the solvent (the remaining solvent after removing the solvents combined in liquids 1 and 2) with constant molar concentration and refractive index. Light speed in a vacuum is *c* and light speed in the solution is *v*, so the light speedsarev_1, v_2, andv_3 in the liquids, respectively. The molar concentrations of solutes$X_1$and X_2 are $p_1$mol/L and $p_2$mol/L.

For the ternary system solution unit volume, it is assumed here that the liquid volume with known molar concentration, known refractive index, and unique solute X_1 is V_1. The liquid volume with known molar concentration, known refractive index, and unique solute $X_2$is V_2, and the rest of the solute volume is V_3. The total distance of light passing through the solution is *L*and the total time is *T*. The distances in liquid 1, liquid2, and liquid3, are L_1, L_2, and$L_3$and the times are T_1, T_2, and T_3, respectively.

The qualities of solute X_1 andX_2 in the solution are the same as those in liquids 1and2, so:

$$p_1\left(V_1 + V_2 + V_3\right) = kV_1 \tag{2}$$

$$p_2\left(V_1 + V_2 + V_3\right) = kV_2 \tag{3}$$

$$p_1 = k\frac{V_1}{V_1 + V_2 + V_3} \tag{4}$$

$$p_2 = k\frac{V_2}{V_1 + V_2 + V_3} \tag{5}$$

$$L_1 = L\frac{V_1}{V_1 + V_2 + V_3} = \frac{Lp_1}{k} \tag{6}$$

$$L_2 = \frac{Lp_2}{k} \tag{7}$$

$$L_3 = \frac{L\left(1 - p_1 - p_2\right)}{k} \tag{8}$$

$$t_1 = \frac{Lp_1}{kv_1} \tag{9}$$

$$t_2 = \frac{Lp_2}{kv_2} \tag{10}$$

$$t_3 = \frac{L(1 - p_1 - p_2)}{kv_3} \tag{11}$$

$$T = \frac{L[p_1v_2v_3 + p_2v_1v_3 + (1 - p_1 - p_2)v_1v_2]}{kv_1v_2v_3} \tag{12}$$

$$v = \frac{L}{T} = \frac{kv_1v_2v_3}{p_1v_2v_3 + p_2v_1v_3 + (1 - p_1 - p_2)v_1v_2} \qquad (13)$$

As for the refractive index n,

$$n = \frac{c}{v} = \frac{c[p_1v_2v_3 + p_2v_1v_3 + (1 - p_1 - p_2)v_1v_2]}{kv_1v_2v_3} = p_1\frac{(cv_3 - cv_1)}{kv_1v_3} + p_2\frac{(cv_3 - cv_2)}{kv_2v_3} + \frac{c}{kv_3} \quad (14)$$

As shown in Eq.(14), the refractive index varies linearly with molar concentrations in the ternary system solution. The solution's refractive index change rate, which is a result of changes in the molar concentrations of the two solutes, depends on the solution properties: Namely, the speed of light in the solution ($k$mol/L).

Experimental Verification

Experimental Methods and Data Collection

The refractive index of the ternary system solution containing two typical solutes ($CuSO_4$-NaCl-H_2O) was measured to verify the model discussed above. There were six solution groups ($CuSO_4$-NaCl-H_2O) with 36 kinds of molar concentrations under analysis. The$CuSO_4$ and NaCl samples were analytically pure ($\geq$99.9%). $CuSO_4$ and NaCl molar concentrations varied from 0-0.5 mol/L at change rate of 0.1 mol /L. The temperature was18.5℃ ($\pm$0.5℃), and a 589nm sodium light served as the light source. A 2W Abbe refracttometer (Shanghai Optical Instrument Factory) was used to measure the refractive index of the six solution groups ($CuSO_4$-NaCl-H_2O) with 36 molar concentrations. The measurement results are shown in Table 1.
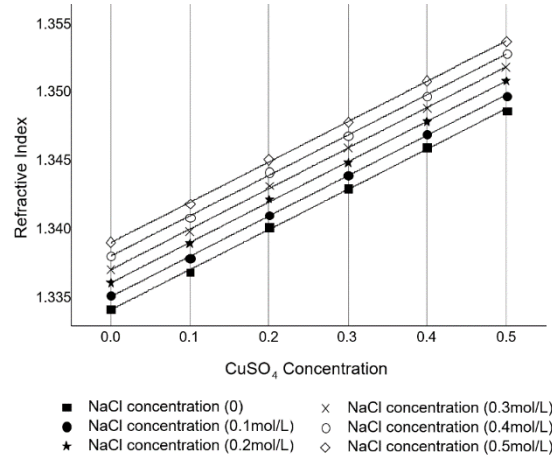
Table 1 Refractive indexes of $CuSO_4$-NaCl-H_2O with different molar concentrations

		NaCl(mol/L)					
		0	0.1	0.2	0.3	0.4	0.5
	0	1.3342	1.3352	1.3361	1.3371	1.3381	1.3391
	0.1	1.3369	1.3379	1.3390	1.3399	1.3409	1.3419
$CuSO_4$ (mol/L)	0.2	1.3402	1.3411	1.3422	1.3432	1.3442	1.3451
	0.3	1.3430	1.3440	1.3449	1.3460	1.3469	1.3479
	0.4	1.3460	1.3470	1.3479	1.3489	1.3498	1.3509
	0.5	1.3487	1.3498	1.3509	1.3519	1.3529	1.3538

Data Analysis

The relationship between the mixed liquid refractive index and the$CuSO_4$ and NaCl molar concentrations determined by processing the above data via linear regression is illustrated in Fig. 2. Coefficient R^2above 0.999 was considered to indicate a close linear fit. Regardless of changes in$CuSO_4$ or NaCl molar concentration, the refractive index of $CuSO_4$-NaCl-H_2O solution varied linearly. In addition, these changes had no significant effect on the refractive index in accordance with the proposed model.

The$CuSO_4$-NaCl-H_2O solution contained NaCl solution (1 mol/L)and $CuSO_4$ solution (1 mol/L);liquids 1and 2were selected with known molar concentrations and a known refractive index. The actual refractive index of the NaCl solution (1 mol/L), CuSO4 solution (1 mol/L), and deionized water comprised the benchmark. The refractive indexes of the ternary system solutions with different molar concentrations were calculated accordingly. The calculated and experimental results were in accordance, with a mean relative error of5.56×10^{-5}.Thisconfirms the feasibility and effectiveness of the proposed equivalent analysis and mathematical modeling technique for ternary system solution refractive indexes.

Fig. 2 Relationship between refractive index of $CuSO_4$-NaCl-H_2O and molar concentration of $CuSO_4$

Refractive Index Multi component Solution Analysis

The relationship between the *N*-ary solution's refractive index and each solute's molar concentration was analyzed based on assessment of the ternary system solution's refractive index and subsequent experimental verification. The *N*-ary solution was regarded as a combination of *N* kinds of liquids with constant molar concentrations and refractive indexes. Liquid 1, liquid 2, and liquid (*N*-1)were considered to be solutions with constant molar concentrations and refractive indexes which combine intosolutesX_1, andX_2, respectively. The molar concentration of liquid *m* (*m* $\in$ [1, *N*-1]) is *k*mol/L. Liquid *N* is a solvent with constant molar concentration and refractive index (the remaining solvent after removing what was combined in liquid 1, liquid 2, and liquid (*N*-1)).

Light speed in a vacuum is *c*, light speed in the solution is *v*, light speed in liquid *m* is v_m, and the solute's molar concentration X_m is p_m*mol/L*. For a unit volume in *N*-ary solution, it is assumed that the liquid volume with known refractive index and molar concentration is V_m and the remaining solvent volume is V_N. The distance of light passing through the solution is *L*and the total time is *T*; the distance of light passing through the liquid *m* is L_m and the time is t_m.

The quality of solute X_m in the solution is the same as that in liquid *m*, thus:

$$p_m V = kV_m \qquad (15)$$

$$p_m = k\frac{V_m}{V} \qquad (16)$$

$$L_m = \frac{Lp_m}{k} \qquad (17)$$

$$L_N = \frac{L\left(1-\sum_{i=1}^{N-1}p_i\right)}{k} \qquad (18)$$

$$t_m = \frac{Lp_m}{kv_m} \qquad (19)$$

$$t_N = \frac{L\left(1-\sum_{i=1}^{N-1}p_i\right)}{kv_N} \qquad (20)$$

$$T = \sum_{i=1}^{N-1}\frac{Lp_i}{kv_i} + \frac{L\left(1-\sum_{i=1}^{N-1}p_i\right)}{kv_N} \qquad (21)$$

$$n = \frac{c}{v} = \frac{Tc}{L} = \sum_{i=1}^{N-1} \frac{cp_i}{kv_i} + \frac{c\left(1 - \sum_{i=1}^{N-1} p_i\right)}{kv_N} = \sum_{i=1}^{N-1} p_i \frac{c(v_N - v_i)}{kv_i v_N} + \frac{c}{kv_N} \tag{22}$$

The refractive index is linearly related to the molar concentrations of (*N*-1) solutes for *N*-ary solution. The molar concentration change rate is dependent on the light speeds in (*N*-1) liquids v_m($m \in [1, N-1]$).

The above equation can also be writtenas follows:

$$n = \sum_{i=1}^{N-1} \frac{cp_i}{kv_i} = \sum_{i=1}^{N} \frac{cV_i}{v_i V} = \sum_{i=1}^{N} \frac{v_i V_i}{v_i V} + \sum_{i=1}^{N} \frac{(c - v_i)V_i}{v_i V} = 1 + \sum_{i=1}^{N} p_i \frac{(c - v_i)}{kv_i} \tag{23}$$

where c is light speed in a vacuum, p_i is the solute's molar concentration X_m, v_i is light speed in the solute with constant molar concentration of $k$mol/L and constant refractive index, v_N is light speed in the solution, and k is the liquid molar concentration with constant molar concentration and refractive index.

Conclusion

In this study, a multi-component solution was modeled and deduced according to the time necessary for monochromatic light to pass through the medium. The multi component system refractive index was found to be linearly related to each solute's molar concentration. A detailed correlation model of the multi-component solution refractive index was proposed, and the model was verified by a ternary system solution experiment. It is important to note that the model was established without considering the interaction between solute ions, and thus would not work well for a solution in which volume is significantly reduced after dissolution (e.g., water and ethanol). Further research is needed to make the necessary volume change correction.

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