Table (2) K_X^{AD} obtained by Equations (3), (4) and (5) from refractometry measurements for the carbon tetrachloride and toluene in cyclohexane at 25 °C.

Applied Method	K_X^{AD}
Equation (3)	-0.602
Equation (4)	-0.667
Equation (5)	-0.620

Table (3 K_X^{AD} calculated by Equations (7) from refractometry and NMR results for the carbon tetrachloride and toluene in cyclohexane at 25°C and the exact value of K_X^{AD} from NMR results related to the gasous state.

	References		
	Cyclohexane (Internal)	TMS (Internal)	NMR (*)
K_X^{AD}	3.4850	3.2787	4.732

(*) The exact calculated value of K_X^{AD} in NMR measurements related to the gaseous state [14].

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$$\delta = \frac{X_D^0 - X_{AD}}{X_D^0}\delta_D + \frac{X_{AD}}{X_D^0}\delta_{AD} \qquad (6)$$

Various equations and similar to those for refractometry measurements, have been obtained by combination of Equations (2) and (6) for the treatment of NMR result and to evaluate K_X^{AD} [4].

Comparison of the results obtained for the same system (toluene/carbon tetrachloride/cyclohexane) by NMR measurements also indicates disagreement between the values of K_X^{AD} by refractometry and NMR methods. It seems that in most cases the disagreement is centered around the problem of separating the products of ($K_X^{AD}k$) in refractometry measurement and ($K_X^{AD}\Delta_{AD}$) in NMR measurements [19] resulting from the slope and intercept evaluations at concentrated or dilute solutions.

To avoid this problem, an equation was derived by substituting for X_{AD} from equations (1) and (6) in Equation (2) to obtain:

$$X_A^0 + X_D^0 - \frac{\Gamma}{k} = \Delta_{AD}\left(\frac{X_D^0}{\Delta}\right) - \frac{1}{K_X^{AD}} \qquad (7)$$

where $\Delta = \delta - \delta_D$ and $\Delta_{AD} = \delta_{AD} - \delta_D$. δ is the measured chemical shift of aromatic ring of toluene in the mixture, δ_D is the chemical shift of D in the solvent and δ_{AD} which is not a measurable quantity is the chemical shift of complex in the solvent. All these chemical shifts are related to the internal reference TMS and cyclohexane.

According to the Equation (7), a plot of the left-hand side of this equation against the values of $\frac{X_D^0}{\Delta}$ should be linear. The K_X^{AD} and k are evaluated respectively from intercept and slope of this plot. Equation (7) has the following advantages: (i) it is not necessary that $X_A^0 >> X_D^0$ and can be used under any conditions, and (ii) K_X^{AD}, can be calculated directly without recourse to extrapolation at infinite concentration.

To treat the results, an iteration procedure based on a least square computer program was used which calculated the left-hand side of Equation (7) to find the best fit to a straight line. Table (3) shows a good agreement between the obtained K_X^{AD}'s for the two references (TMS and cyclohexane).

On comparing the results of K_X^{AD} calculated by Equation (7), it is clear that, they are in good agreement with the exact results obtained for K_X^{AD} in previous work (14) in which the measured NMR chemical shifts were related to the gaseous state and therefore the undesirable side effects were eliminated.

Table (1)The deviations of refractive index of mixtures from linearity (Γ) and the differences between the measured chemical shifts (Hz) of *D* in solvent and in mixture with *A* (Δ) for carbon tetrachloride and toluene in cyclohexane at 25°C.

Mole fraction Toluene	CCL_4	$\Gamma \times 10^4$	Δ (Hz)
0.029	0.000		
	0.120	0.947	0.399
	0.226	1.940	0.685
	0.425	4.356	1.398
	0.630	8.076	2.249

and the electron acceptor A, (neglecting the solvent effects). If it is assumed that the deviation is entirely due to the molecular interactions which result in a charge transfer complex formation between D and A, then the deviation should be proportional to the concentration of the complex in the mixture. Therefore the deviations of the refractive index from linearity (Γ) for a mixture of D and A in solvent, the following proportionality can be written [17].

$$\Gamma = kX_{AD} \tag{1}$$

where k is a constant and X_{AD} is the mole fraction of complex.

Under experimental condition where the acceptor is in large excess over the donor and the mole fraction of donor (X is sufficiently small, for the case of 1:1 complex formation of the form:

$$A + D = AD$$

the mole fraction stability constant K_X^{AD} may be approximated as:

$$K_X^{AD} = \frac{X_{AD}}{(X_D^0 - X_{AD})X_A^0} \tag{2}$$

where X_D^0 and X_A^0 indicate the total, *i.e.* free and complexed, mole fractions of D and A respectively. From a combination of equation (1) and (2), the following equation can be obtained:

$$\frac{\Gamma}{X_A^0 X_D^0} = kK_X^{AD} - K_X^{AD}\Gamma \tag{3}$$

Also further rearrangement of Equation (3) gives:

$$\frac{X_D^0}{\Gamma} = \frac{1}{kK_X^{AD}}\frac{1}{X_A^0} + \frac{1}{k} \tag{4}$$

$$\frac{X_A^0 X_D^0}{\Gamma} = \frac{X_A^0}{k} + \frac{1}{kK_X^{AD}} \tag{5}$$

These equations, which are based on the simple linear relationships, can be used to evaluate K_X^{AD}. The calculated stability constants by these equations is reported in Table (2). The negative and near zero values of stability constant obtained from these equations can be attributed to the shortcomings of equations (3), (4) and (5) since they are based on linear plots and they need extrapolation to infinitely diluted or infinitely concentrated solutions to evaluate K_X^{AD} from the slope or intercept of the plots.

In the case of NMR measurements the measured chemical shift (δ) is the population average of the shifts due to pure D (δ_D) and pure complex AD (δ_{AD}) in all solutions according to the following Equation [18]:

Correlation of NMR and Refractometry Results to Evaluate the Stability Constant of Carbon Tetrachloride Complexes

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Abstract

An equation has been suggested which correlate the NMR and refractometry results to evaluate the stability constant of electron donor acceptor complexes. Using this equation the stability constant of complexation between carbon tetrachloride and toluene in cyclohexane has been studied by refractometry and NMR spectroscopy.

Key words

Charge-transfer Complexes; Stability constant; NMR Spectroscopy, Refractometry, Carbontetrachloride

Introduction

The study of charge-transfer complexes has attracted much attention over the past years. These complexes have been examined by various experimental methods including vapor pressure osmometry [1,2], conductometry [3], gas liquid chromatography [4-6], ultra violet-visible spectroscopy [7] infrared spectroscopy [9,10], fluorescence spectroscopy[11,12] and nuclear magnetic resonance (NMR) spectroscopy [13-15]. In addition to the above techniques, there are other methods that are less expensive but with the same effectiveness and accuracy, refractometry [16,17] is among these techniques.

Carbon tetrachloride is known as an inert solvent because ideal behaviour is expected for its mixture with aromatic compounds. However, investigation on the solutions containing carbon tetrachloride showed evidences of complex formation [14]. In this work the formation constant of carbon tetrachloride complexes has been studied by both refractometry and NMR spectroscopy. Also a new equation has been suggested for correlating refractometry and NMIR results.

1-Experimental

The solutions preparation and experimental procedure in NMR measurements have been described in the previous work [14]. The results of NMR chemical shift measurements are reported in Table (1). The refractive indices of solutions have been measured using Abbe refractometer at 25°C. The temperature of solutions was maintained constant (±0.1°C) by a circulating water thermostat. The refractometry results also are reported in Table (1).

The reagent grade carbon tetrachloride, toluene and cyclohexane (obtained from Merck Company) have been used without further purification.

2-Discussion

It is a well accepted assumption that the non-linear plot of any physical property of a mixture against its composition is an indication of deviation from ideal behaviour which arises from the interactions between the species in the mixture namely the electron donor *D*,