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Table (5) The bulk magnetic susceptibility correction (Hz) for external references (TMS, CXA, HMDS) for $[AgNO_3(A) / C_6H_5 - CH_2 - C \equiv N (D) / (CH_2OH)_2]$

mixtures for the case $X_D^0 \gg X_A^0$ at 20 °C.

X_D^0	δ_{corr} (TMS)	δ_{corr} (CXA)	δ_{corr} (HMDS)
0.715	12.315	17.527	13.762
0.821	13.176	18.321	14.157
0.873	14.712	18.742	14.963
0.931	14.937	19.325	15.231
0.956	15.125	19.963	15.863
0.976	15.832	20.563	15.998
1.000	16.105	21.763	16.231

Table (6) The calculated parameters of Debye-Huckel mean ionic activity coefficient for $AgNO_3$ in $[AgNO_3(A) / C_6H_5 - CH_2 - C \equiv N (D) / (CH_2OH)_2]$ mixtures at 20 °C.

Calculated:	α	β
by Eq. 14	-0.763	0.012
by Eq. 33	-0.535	0.032

Table (7) The calculated formation constants, using the measured chemical shifts against external references, on molarity (C), mole fraction (X) and molality (m) by Eq. (5) for the case $X_D^0 \gg X_A^0$ at 20 °C.

Ext.Ref.	K_{AD}^C	K_{AD}^X	K_{AD}^m	K_{AD}^X / K_{AD}^C	K_{AD}^X / K_{AD}^m
TMS	0.319	2.04	0.230	6.394	8.870
CXA	0.230	1.82	0.210	7.913	8.667
HMDS	0.220	1.60	0.220	7.272	7.273

Table (8) The calculated formation constants, using the measured chemical shifts against external references, on molarity (C), mole fraction (X) and molality (m) by Eq. (5) for the case $X_D^0 \gg X_A^0$ at 20 °C.

Ext.Ref.	K_{AD}^C	K_{AD}^X	K_{AD}^m	K_{AD}^X / K_{AD}^C	K_{AD}^X / K_{AD}^m
TMS	1.267	13.412	9.315	10.586	1.440
CXA	1.531	14.373	7.421	9.388	1.937
HMDS	1.723	15.682	8.678	9.103	1.807

Table (9) The calculated formation constants, using the measured chemical shifts against external references, by Eq.s (8), (27) and (33).

Ext. Reference	Eq. 8	Eq. 27	Eq. 33
TMS	0.221	0.207	0.273
CXA	0.242	0.213	0.272
HMDS	0.231	0.214	0.271

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Table (1) The measured chemical shifts (Hz) of CH_2 - groups of $(CH_2OH)_2$ in $[AgNO_3/(CH_2OH)_2]$ mixtures against external references (TMS, CXA, HMDS) at 20 °C. ($X_A^0 = AgNO_3$ mole fraction).

X_A^0	TMS	CXA	HMDS
0.015	257.247	259.329	257.805
0.032	257.334	259.470	257.969
0.047	257.632	259.740	258.184
0.063	257.84	259.929	258.391
0.093	258.237	260.355	258.832
0.125	258.638	260.762	259.159

Table (2) The measured chemical shifts(Hz) of aromatic group of benzylcyanide in $[C_6H_5 - CH_2 - C \equiv N / (CH_2OH)_2]$ mixtures against external references (TMS, CXA, HMDS) at 20 °C. ($X_D^0 =$ benzylcyanide mole fraction).

X_D^0	TMS	CXA	HMDS
0.750	776.341	614.321	753.214
0.810	778.422	614.732	756.218
0.863	783.241	615.120	757.102
0.912	787.317	615.720	758.216
0.932	789.324	615.832	759.312

Table (3) The measured chemical shifts(Hz) of aromatic group of benzylcyanide in $[AgNO_3 (A) / C_6H_5 - CH_2 - C \equiv N (D) / (CH_2OH)_2]$ mixtures against external references (TMS, CXA, HMDS) at 20 °C for cases $X_A^0 \gg X_D^0$ and $X_D^0 \gg X_A^0$.

$X_A^0 \gg X_D^0$				$X_D^0 \gg X_A^0$			
$X_D^0 = 0.005$				$X_A^0 = 0.005$			
X_A^0	TMS	CXA	HMDS	X_D^0	TMS	CXA	HMDS
0.00	776.103	614.501	764.522	0.715	771.521	615.412	767.231
0.013	777.604	616.180	766.201	0.821	775.371	615.813	769.352
0.034	780.213	618.773	768.816	0.873	783.314	615.971	770.481
0.048	782.472	620.809	770.594	0.931	792.452	616.135	770.827
0.064	783.883	622.742	772.379	0.956	795.631	616.317	771.316
0.097	788.270	626.959	776.518	0.976	797.712	616.513	771.792
0.134	793.20	629.700	781.921	1.00	798.432	616.723	771.983

Table (4) The bulk magnetic susceptibility correction (Hz) for external references (TMS, CXA, HMDS) for $[AgNO_3 (A) / C_6H_5 - CH_2 - C \equiv N (D) / (CH_2OH)_2]$ mixtures for the case $X_A^0 \gg X_D^0$ at 20 °C.

X_A^0	δ_{corr} (TMS)	δ_{corr} (CXA)	δ_{corr} (HMDS)
0.00	32.028	27.004	25.012
0.013	32.174	27.151	25.793
0.034	32.404	27.380	25.982
0.048	32.551	27.526	26.137
0.064	32.739	27.716	26.513
0.097	33.116	28.093	26.712
0.134	33.353	28.513	26.941

Conclusion

In the formation constants evaluation for the charge transfer complexes by various methods usually several difficulties are encountered which cause one to cast doubt about the validity and the true meaning of the values reported for the formation constants. In this work NMR spectroscopy measurements for evaluation of the formation constant of charge transfer complexes is examined and the inherent difficulties in the method is elucidated. The difficulties such as the shortcomings of the previous equations, i.e. separating the effect of the complex formation reaction on the chemical shifts from the other effects, the internal referencing, concentration scales, concentration domain and the solution nonidealities have been discussed.

New equations have been suggested for application in different concentration domain and then these equations have been corrected for the solution nonidealities.

It is left to the future work to examine the extension and application of the proposed equations to the other complex forming mixtures.

Appendix

For the case $[D]_0 \gg [A]_0$ the K_{AD}^X / K_{AD}^C is in the range:

$$\frac{1}{\bar{V}_S + X_{D_{\max}}^0 (\bar{V}_D - \bar{V}_S)} < \frac{K_{AD}^X}{K_{AD}^C} < \frac{1}{\bar{V}_S + X_{D_{\min}}^0 (\bar{V}_D - \bar{V}_S)} \quad \bar{V}_D > \bar{V}_S$$

$$\frac{1}{\bar{V}_S + X_{D_{\min}}^0 (\bar{V}_D - \bar{V}_S)} < \frac{K_{AD}^X}{K_{AD}^C} < \frac{1}{\bar{V}_S + X_{D_{\max}}^0 (\bar{V}_D - \bar{V}_S)} \quad \bar{V}_D < \bar{V}_S$$

For the case $[A]_0 \gg [D]_0$ the K_{AD}^X / K_{AD}^C is in the range:

$$\frac{1}{\bar{V}_S + X_{A_{\max}}^0 (\bar{V}_A - \bar{V}_S)} < \frac{K_{AD}^X}{K_{AD}^C} < \frac{1}{\bar{V}_S + X_{A_{\min}}^0 (\bar{V}_A - \bar{V}_S)} \quad \bar{V}_A > \bar{V}_S$$

$$\frac{1}{\bar{V}_S + X_{A_{\min}}^0 (\bar{V}_A - \bar{V}_S)} < \frac{K_{AD}^X}{K_{AD}^C} < \frac{1}{\bar{V}_S + X_{A_{\max}}^0 (\bar{V}_A - \bar{V}_S)} \quad \bar{V}_A < \bar{V}_S$$

For the case $[D]_0 \gg [A]_0$ the K_{AD}^X / K_{AD}^m is in the range:

$$\frac{1000}{M_S(1 - X_{D_{\min}}^0)} < \frac{K_{AD}^X}{K_{AD}^m} < \frac{1000}{M_S(1 - X_{D_{\max}}^0)}$$

For the case $[A]_0 \gg [D]_0$ the K_{AD}^X / K_{AD}^m is in the range:

$$\frac{1000}{M_S(1 - X_{A_{\min}}^0)} < \frac{K_{AD}^X}{K_{AD}^m} < \frac{1000}{M_S(1 - X_{A_{\max}}^0)}$$

where $X_{A_{\max}}^0$ and $X_{D_{\max}}^0$ are respectively the maximum mole fractions of A and D. $X_{A_{\min}}^0$ and $X_{D_{\min}}^0$ are respectively the minimum mole fraction in the concentration domain used in the studied mixtures.

$$\begin{aligned}\Delta^I &= \delta_D^{(I)avg} - \delta_D^\infty \\ \Delta^{II} &= \delta_D^{(II)avg} - \delta_D^0\end{aligned}\quad (28)$$

From Eq. (27), K_{AD} can be calculated directly from the slope of a plot of the values on the left hand side vs. the values on the right hand side. These values are all measurable quantities. Eq. (27) has the added advantage that it does not contain the unmeasurable chemical shift of complex δ_{AD} and thus the need for extrapolation, which is major problem in Eq.s (3), (4) and (5) have been eliminated. The corrected chemical shifts for the bulk magnetic susceptibilities were used in Eq. (27). The results are tabulated in the Table (9).

5- Extending the new Eq. for nonideal behavior

On the basis of above discussion, the expression for K_{AD} for the case where, $[A]_0 \gg [D]_0$, is:

$$K_{AD} = \frac{a_{AD}^{(I)}}{a_D^{(I)} a_A^{(I)}} = \frac{(X_{AD} \gamma_{AD}^{(H)})^{(I)}}{(X_D \gamma_D^{(H)})^{(I)} (m_A^2 \gamma_{\pm A}^2)^{(I)}} \quad (29)$$

Since K_{AD} and $X_D^{(I)}$ are small the Henry's law activity coefficients are close to unity, then $\gamma_{AD}^{(H)} \cong \gamma_D^{(H)} \cong 1$. Therefore:

$$K_{AD} = \frac{X_{AD}^{(I)}}{X_D^{(I)} (m_A^2 \gamma_{\pm A}^2)^{(I)}} \quad (30)$$

For the case where $[D]_0 \gg [A]_0$:

$$K_{AD} = \frac{a_{AD}^{(II)}}{a_D^{(II)} a_A^{(II)}} = \frac{(X_{AD} \gamma_{AD}^{(H)})^{(II)}}{(X_D \gamma_D^{(R)})_0^{(II)} (m_A^2 \gamma_{\pm A}^2)_0^{(II)}} \quad (31)$$

In this case X_{AD} and m_A are small. Therefore the activity coefficients of Henry's law are: $\gamma_{AD}^{(H)} \cong 1$ and the activity coefficient of Debye-Huckel law is $\gamma_{\pm} \cong 1$. Since $X_D^{(II)} \cong 1$, D obeys the Raoult's law and the $\gamma_D^{(R)} \cong 1$. In this case K_{AD} can be presented:

$$K_{AD} = \frac{X_{DA}^{(II)}}{X_D^{(II)} (m_A^2)_0^{(II)}} \quad (32)$$

where in Eq. (30) and (32) symbols (I) and (II) used to indicate difference in concentration domain.

On combining (32), (30), (23) and (25) and after rearrangement the following equation is obtained:

$$\begin{aligned}(m_A^2)_0^{(II)} \Delta^{(II)} - (m_A^2 \gamma_{\pm A}^2)_0^{(I)} \Delta^{(II)} = \\ K_{AD} \{ \Delta^{(I)} (m_A^2 \gamma_{\pm A}^2)_0^{(I)} + \Delta^{(II)} (m_A^2 \gamma_{\pm A}^2)_0^{(I)} (X_D)_0^{(II)} - \delta_D^\infty (m_A^2 \gamma_{\pm A}^2)_0^{(I)} (X_D)_0^{(II)} \}\end{aligned}\quad (33)$$

A least square based computer program used to calculate K_{AD} . In the program γ_{\pm} was calculated via Eq. (18) for inserted values of α and varying values of β . The results are reported in Table 9.

reported respectively in Tables 7 and 8. The molar volume of benzylocyanide at 20 °C is: $\bar{V}_D = 16.886 \text{ cm}^3/\text{mol}$ and its molar mass is: $M_D = 117.14 \text{ g/mol}$. The molar volume of solvent ethylene glycol at 20 °C is: $\bar{V}_S = 5.584 \text{ cm}^3/\text{mol}$ and its molar mass is: $M_S = 62.07 \text{ g/mol}$. Our laboratory experimental measurements on the partial molar volumes of $[\text{AgNO}_3/(\text{CH}_2\text{OH})_2]$ indicated that in the range of concentration variations of AgNO_3 , the partial molar volumes of AgNO_3 are 6.2×10^{-6} to $7.0 \times 10^{-2} \text{ cm}^3/\text{mol}$ at 20 °C. From the results in Table 3 and the equations in the Appendix for the case $X_D^0 \gg X_A^0$: ($59.2 < K_{AD}^{(X)} / K_{AD}^{(C)} < 73.2$) and ($56.5 < K_{AD}^{(X)} / K_{AD}^{(m)} < 161.1$) and for the case $X_A^0 \gg X_D^0$: ($181.4 < K_{AD}^{(X)} / K_{AD}^{(C)} < 206.8$) and ($16.3 < K_{AD}^{(X)} / K_{AD}^{(m)} < 18.6$). Therefore it is seen from the results in Tables 7 and 8 that K_{AD} s on different concentration scales are not in agreement with these values for the two reported cases: $[A]_0 \gg [D]_0$ and $[D]_0 \gg [A]_0$ and it becomes evident that the K_{AD} s are dependent not only on the concentration scales but are also dependent on the chosen concentration domain.

4- New equation for ideal behavior

The average chemical shift for D (δ_D^{avg}) can be expressed in terms of the chemical shift in the complexed form (δ_{AD}) and in the uncomplexed form (δ_D) [35]:

$$\delta_D^{avg} = ([AD]/[D]_0)\delta_{AD} + \{([D]_0 - [AD])/[D]_0\}\delta_D \quad (23)$$

On combining the above equation with Eq. (16) gives for the case $[A]_0 \gg [D]_0$,

$$\delta_D^{(I)avg} = \frac{K_{AD}[D]_0^{(I)}}{1 + K_{AD}[A]_0^{(I)}}(\delta_{AD} - \delta_D^\infty) + \delta_D^\infty \quad (24)$$

where δ_D^∞ is the chemical shift of D at infinite dilution.

For the case where $[D]_0 \gg [A]_0$, the $\delta_D^{(II)}$ is expressed as:

$$\delta_D^{(II)avg} = \frac{[AD]_0^{(II)}}{[D]_0^{(II)}}\delta_{AD} + \delta_D^0 \quad (25)$$

On combining Eq. (25) with Eq. (17), gives:

$$\delta_D^{(II)avg} = \frac{K_{AD}[A]_0^{(II)}}{1 + K_{AD}[A]_0^{(II)}}\delta_{AD} - \delta_D^0 \quad (26)$$

where δ_D^0 is the chemical shift of D at infinite concentration.

It also should be noted that superscript (I) and (II) were used in Eq. (24) and (26) is to emphasize the difference of concentration domain.

On substituting for δ_{AD} from Eq. (26) in (24) it is straightforward to show that the following equation will be obtained:

$$[A]_0^{(II)}\Delta^I - [A]_0^{(I)}\Delta^{II} = K_{DA}\{\Delta^I[A]_0^I + \Delta^{II}[A]_0^{II} - \delta_D^\infty[A]_0^I[D]_0^{II}\} \quad (27)$$

where (I) and (II) refers to the concentration domain of Eq. (24) and (26) respectively, and Δ^I and Δ^{II} are defined as:

reference used and this proved the effectiveness of the suggested equation.

In this work we follow our previous procedure and propose a new equation for evaluation of K_{AD} from NMR results for the mixture system under investigation:

3-The concentration domain

In NMR study of complex formation, to simplify the equations used in the calculations, it is usual to consider two cases of concentration domain [31]: case (I): $[A]_0 \gg [D]_0$ and case (II): $[D]_0 \gg [A]_0$

The case (I): where the concentration of acceptor in an arbitrary concentration scale is much higher than that of the donor $[A]_0 \gg [D]_0$ and then the formation constant can be expressed as:

$$K_{AD} = \frac{[AD]^I}{([D]_0 - [AD]^I)[A]_0^I} \quad (16)$$

The case (II): where the concentration of the donor is much higher than that of the acceptor $[D]_0 \gg [A]_0$ and the formation constant can be expressed as:

$$K_{AD} = \frac{[AD]^{II}}{([A]_0^{II} - [AD]^{II})[D]_0^{II}} \quad (17)$$

The following relationships can be developed between K_{AD} 's calculated on different concentration scales for both cases:

$$K_{AD}^{(X)} = \frac{K_{AD}^{(C)}}{V_S + X_D^0 (\bar{V}_D - \bar{V}_S)} \quad (\text{for } [D]_0 \gg [A]_0) \quad (18)$$

$$K_{AD}^{(X)} = \frac{K_{AD}^{(C)}}{V_S + X_A^0 (\bar{V}_A - \bar{V}_S)} \quad (\text{For } [A]_0 \gg [D]_0) \quad (19)$$

$$K_{AD}^{(X)} = \frac{1000 K_{AD}^{(m)}}{M_S (1 - X_D^0)} \quad (\text{For } [D]_0 \gg [A]_0) \quad (20)$$

$$K_{AD}^{(X)} = \frac{1000 K_{AD}^{(m)}}{M_S (1 - X_A^0)} \quad (\text{For } [A]_0 \gg [D]_0) \quad (21)$$

where X , C and m are used to represent respectively the mole fraction, molarity and molality concentration scales. \bar{V}_A , \bar{V}_D and \bar{V}_S are respectively molar volumes of A , D and solvent (S) and M_S is the molecular weight of solvent.

If X_D^0 or X_A^0 are small, the following approximations are obtained from the above equations:

$$K_{AD}^{(X)} / K_{AD}^{(C)} = \frac{1}{V_S} \quad \text{and} \quad K_{AD}^{(X)} / K_{AD}^{(m)} = \frac{1000}{M_S} \quad (22)$$

The range of variation of the $K_{AD}^{(X)} / K_{AD}^{(C)}$ and $K_{AD}^{(X)} / K_{AD}^{(m)}$ are presented in the Appendix.

The K_{AD} values calculated by Eq. (5) for the cases $[A]_0 \gg [D]_0$ and $[D]_0 \gg [A]_0$ are

$$\log\left[\frac{\Delta m_A^{**2}}{\Delta^{**} m_A^2}\right]/(m_A - m_A^{**}) = \alpha \frac{m_A^{1/2} - m_A^{**1/2}}{m_A - m_A^{**}} + \beta \quad (14)$$

The values of parameters α and β can be obtained respectively from the slope and intercept of the plot of the values on the left hand side of the above equation versus $\frac{m_A^{1/2} - m_A^{**1/2}}{m_A - m_A^{**}}$. The results are reported in Table 6.

The K_{AD} evaluated by Eq. (8), using the corrected chemical shifts and the mean ionic activity coefficients are reported in Table 8.

Discussion

1- The concentration scales

There is considerable discussion on the problem of which concentration scale should be used for expressing the equilibrium constants (here, named formation constant and shown as K_{AD}). On the theoretical basis, it has been suggested that molarity is a correct concentration scale, as reactions generally involve energy change which is directly related to intermolecular separations, molarities are representative of this separations, while mole fractions are not. On the other hand, thermodynamic behavior of the solution have been derived from kinetic interpretation of the process of evaporation [40] and it is believed that when molecules have the same size and shape, the surface composition can be taken to be the same as internal composition of the solution. Thus the rate of condensation of vapor molecules on the unit area of the liquid surface is proportional to the vapor pressure and on this basis Raoult's law would be expressed on mole fraction units. So, on this basis the correct concentration scale for expressing thermodynamic quantities would be mole fraction.

The results obtained in this work by now, substantiate this suggestion that solution nonidealities are the major cause for the present disagreement in the use of concentration scales. In addition, the results indicate that the proper choice of concentration range, where the activity coefficients are not available for components, can compensate to some extent for the solution nonidealities. However we believe that there are also other factors, which can cause major problems in studying the complexes. These factors include the chemical shift and the concentration domain.

2-The chemical shift

It has been shown that the chemical shift has several components [38]

$$\delta = \delta_a + \delta_b + \delta_s + \delta_c \quad (15)$$

where δ_a , δ_b , δ_s and δ_c are due to the magnetic anisotropy, bulk magnetic susceptibility, solvent effect [41] and complex formation [18] respectively. There are reports that, the other components may have larger contribution in the measured chemical shift than the δ_c which is due to the complex formation. Also internal referencing procedure can cause serious problem since the internal reference may form weak charge transfer complex with the other compounds in the mixture such as A , D and S [18, 41]. If the chemical shift is referred to the gaseous state of the mixtures the undesirable contributions of δ_a , δ_b and δ_s on the measured chemical shifts can be eliminated [18].

In the previous paper it was shown that the measurements of the chemical shift by external referencing procedure can relate the chemical shift to the gaseous state of the mixture and a new equation was suggested [18]. The results indicated that the K_{AD} is independent of the type

The measured chemical shifts Δ are corrected, at each mole fraction, for the bulk magnetic susceptibilities by adding the value of δ_{corr} to them as given by the following equation [36, 37].

$$\delta_{corr}^{(Hz)} = \frac{2\pi}{3}(\chi_s - \chi_A) \times 10^6 \quad \text{and} \quad \delta_{corr}^{(Hz)} = \frac{2\pi}{3}(\chi_s - \chi_D) \times 10^6 \quad (9)$$

where $(\chi_s - \chi_A)$ and $(\chi_s - \chi_D)$ are the bulk magnetic susceptibility differences of solute $AgNO_3$ (A), benzylocyanide (D) and solvent, $(CH_2OH)_2$, (S) respectively.

To evaluate $(\chi_s - \chi_A)$ and $(\chi_s - \chi_D)$ the measured chemical shifts reported in Table 1 and Table 2 are used respectively in the following equations:

$$\frac{\delta' - \delta''}{X' - X''} = \frac{2\pi}{3}(\chi_s - \chi_A) \times 10^6 \quad \text{and} \quad \frac{\delta' - \delta''}{X' - X''} = \frac{2\pi}{3}(\chi_s - \chi_D) \times 10^6 \quad (10)$$

where δ' and δ'' are the chemical shifts of CH_2 group of ethylene glycol or aromatic group of benzylocyanide respectively in two mole fractions X' and X'' .

The calculated values of corrections on the chemical shifts δ_{corr} are reported in Table 4 and Table 5.

(ii) *Mean ionic activity coefficient evaluation*

From the theory of NMR, for a mixture of $[AgNO_3/(CH_2OH)_2]$ the following equation holds [38]

$$\frac{\Delta}{\Delta^{**}} = \frac{a_A}{a_A^{**}} \quad (11)$$

where Δ represents differences between the chemical shifts of CH_2 - group of ethylene glycol in the mixture with $AgNO_3$, δ , and in the pure state, δ^* i.e. $\Delta = \delta - \delta^*$.

In Eq. (11), Δ^{**} represents the difference between the chemical shift of CH_2 group of ethylene glycol saturated with $AgNO_3$, δ^{**} , and its chemical shift in pure state, δ^* i.e. $\Delta^{**} = \delta^{**} - \delta^*$.

The activities in Eq. (11) can be expressed in terms of molalities and mean ionic activity coefficient in the following form:

$$\frac{\Delta}{\Delta^{**}} = \frac{m_A^2 \gamma_{\pm A}^2}{m_A^{**2} \gamma_{\pm A}^{**2}} \quad (12)$$

The mean ionic activity coefficient for 1:1 electrolyte can be expressed in terms of Debye-Huckel theory [39]:

$$\log \gamma_{\pm A} = \alpha \sqrt{m_A} + \beta m_A \quad (13)$$

On substituting from Eq. (13) in Eq. (12) and after rearrangement the following equation is obtained:

several times shortly before usage to remove the dissolved oxygen.

The chemical shifts were measured from external references tetramethylsilane (TMS), hexamethyldisilane (HMDS) and cyclohexane (CXA) using the side band technique of 100 MHz NMR Varian spectrometer. The mechanics of the external referencing method is simply a spinning coaxial system of two precision glass tubes. The sample to be studied is placed in annular region between the outer diameter of the inner tube and the inner diameter of the outer tube. The standard reference is placed in the inner tube.

When the external reference is used, the interference of reference in the complex formation with the other components of mixture is avoided, however a bulk magnetic susceptibility correction on the measured chemical shift is necessary. This correction has been done on the measured chemical shifts and the procedure leading to evaluation of the required bulk magnetic susceptibility differences of $[AgNO_3/(CH_2OH)_2]$ and $[C_6H_5 - CH_2 - C \equiv N/(CH_2OH)_2]$ will be described in the next section.

Results

The measured chemical shifts of CH_2 - groups of ethylene glycole in the $[AgNO_3/(CH_2OH)_2]$ mixtures are reported in Table 1. The measured chemical shifts of the aromatic group of benzylcyanide in $[(CH_2OH)_2/C_6H_5 - CH_2 - C \equiv N]$ mixtures are reported in Table 2 and the measured chemical shifts of the aromatic group of benzylcyanide in $[AgNO_3/(CH_2OH)_2/C_6H_5 - CH_2 - C \equiv N]$ mixtures are reported in Table 3.

According to Eq. (1) the K_{AD} for the complex formation reaction between $AgNO_3$ (A) and benzylcyanide (D) for the case where $X_A^0 \gg X_D^0$ can be represented as

$$K_{AD} = \frac{X_{AD}\gamma_{AD}^{(H)}}{(X_D^0 - X_{AD})\gamma_D^{(H)}m_A^2\gamma_{\pm A}^2} = \frac{X_{AD}}{(X_D^0 - X_{AD})m_A^2\gamma_{\pm A}^2} \quad (6)$$

where $\gamma_{AD}^{(H)} \cong \gamma_D^{(H)} \cong 1$ since X_D^0 and then X_{AD} are very small and it is reasonable to assume that AD and D have ideal behavior on the Henry's law [32]. In Eq. (6) the activity of 1:1 electrolyte, $AgNO_3$, can be expressed as $a_A = m_A^2\gamma_{\pm A}^2$ [33], where m is the molality and γ_{\pm} is the molality based mean ionic activity coefficient.

According to the modification of McConell [34] on the Gutowsky's equation [35] the following equation can be derived for this case of complex formation:

$$\frac{\Delta}{\Delta_{AD}} = \frac{X_{AD}}{X_D^0} \quad (7)$$

On combining Eq.s (6) and (7) it will be obtained.

$$\frac{\Delta}{m_A^2\gamma_{\pm A}^2} = -K_{AD}\Delta + K_{AD}\Delta_{AD} \quad (8)$$

where m_A and $\gamma_{\pm A}$ respectively denote the molality and mean ionic activity coefficient of $AgNO_3$. According to Eq. (8) a plot of $\Delta/m_A^2\gamma_{\pm A}^2$ versus Δ should be linear and the K_{AD} will be obtained from the slope of this plot.

To use Eq. (8) it is necessary; (i) to correct the measured chemical shifts for the bulk magnetic susceptibilities and (ii) to evaluate the mean ionic activity coefficient of $AgNO_3$.

(i) Bulk magnetic susceptibility correction



The formation constant for this reaction is defined as:

$$K_{AD} = \frac{a_{AD}}{a_A a_D} = \frac{[X_{AD} \gamma_{AD}]}{[(X_A^0 - X_{AD}) \gamma_A][(X_D^0 - X_{AD}) \gamma_D]} \quad (2)$$

where a , γ and X represent the activity, activity coefficient and mole fraction, respectively. In Eq. (2) X_D^0 and X_A^0 denote the initial concentrations. Assuming ideal behavior $\gamma_A \cong \gamma_D \cong \gamma_{AD} \cong 1$ and for the case where $X_A^0 \gg X_D^0$ the following Eq.s have been derived to evaluate K_{AD} from the measured chemical shifts Δ in NMR spectroscopy measurements.

$$\frac{1}{\Delta} = \frac{1}{K_{AD}} \frac{1}{\Delta_{AD}} \frac{1}{X_A^0} + \frac{1}{\Delta_{AD}} \quad (3)$$

$$\frac{X_A^0}{\Delta} = \frac{X_A^0}{\Delta_{AD}} + \frac{1}{K_{AD} \Delta_{AD}} \quad (4)$$

$$\frac{\Delta}{X_A^0} = -K_{AD} \Delta + K_{AD} \Delta_{AD} \quad X_A^0 \gg X_D^0 \quad (5)$$

$$\frac{\Delta}{X_D^0} = -K_{AD} \Delta + K_{AD} \Delta_{AD} \quad X_D^0 \gg X_A^0$$

where $\Delta = \delta - \delta^0$, is the difference between the measured chemical shift δ of a nucleus in molecule D in presence of A in a solvent S and the chemical shift of the same nucleus D in the solvent S . In the above equations, Δ_{AD} represents the chemical shift of complex AD and is defined as; $\Delta_{AD} = \delta_{AD} - \delta^0$. It is worth noting that Δ_{AD} is not a measurable quantity and can be calculated from the above equations.

Eq.s (3), (4), and (5) are respectively due to Benesi-Hildebrand [27], Scott [28] and Scatchard [29] and Foster [30]. Among these three equations, Eq. (5) is more reliable in evaluation of K_{AD} since Eq. (1) needs extrapolation to infinite concentration of A ($X_A^0 \rightarrow \infty$) whereas Eq. (4) needs an extrapolation to infinite dilution of A ($X_A^0 \rightarrow 0$).

In this work the formation of charge transfer complexes of silver nitrate ($AgNO_3$) with benzyliyanide ($C_6H_5-CH_2-C \equiv N$) in ethylene glycol [$(CH_2OH)_2$] as the solvent has been studied by NMR spectroscopy. This mixture is of particular interest as the other techniques such as vapor pressure and gas liquid chromatography can be used for similar studies, because $AgNO_3 / (CH_2OH)_2$ mixture form an involatile liquid phase which can be in equilibrium with the dissolved benzyliyanide in the liquid phase and in the vapor phase.

Although the theory of charge transfer complexes has been well formulated it does not provide enough information to specify in the process of charge transfer which molecule acts as the electron donor and which as the electron acceptor. However Pauling [31] suggested that Ag^+ can act as electron acceptor and forms complexes with organic compounds especially with those having π -electron. Therefore, there is obvious reason to believe that benzyliyanide will act as the electron donor in the mixture studied in this work.

Experimental

All the compounds used, were of pure grade and thus no further purification was done on them. The solutions were prepared by mass in 25 ml measuring flasks and were degassed

Nuclear Magnetic Resonance Study of Charge Transfer Complex Formation Between Silver Nitrate and Benzylcyanide in Solvent Ethylene Glycol

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Abstract

The formation constant for charge transfer complexes between electron acceptor (AgNO_3) and electron donor benzylcyanide ($\text{C}_6\text{H}_5 - \text{CH}_2 - \text{C} \equiv \text{N}$) in solvent ethyleneglycol $[(\text{CH}_2\text{OH})_2]$ has been evaluated by using the Nuclear Magnetic Resonance (NMR) chemical shifts of aromatic group of benzylcyanide measured against external referencres, tetrametylsilane (TMS), hexamethyldisilane (HMDS) and cyclohexane (CXA) at 20 °C. The external referencing procedure eliminated the interference of internal reference in the course of complexation. The necessary bulk magnetic susceptibility corrections on the measured chemical shifts have been made. The solution nonidealities and their effects on the formation constant have been considered and a new equation has been suggested to obtain the mean ionic activity coefficient of AgNO_3 from NMR results. The mean ionic activity coefficient has been taken into account in the formation constant calculations. The results indicated that the appropriate formation constant should be expressed in terms of activities. Also an equation have been derived to eliminate the undesirable effects on the NMR measured chemical shifts in calculating the formation constant. The selection of concentration domains and its effect on the calculated formation constant has been discussed and the new equation is modified to be independent of the concentration domains. In this equation the solution nonidealities, by considering the activity coefficients, have been taken into account.

Keywords

formation constant, silver nitrate, benzylcyanide, ethylene glycol, charge transfer complexes, solution nonidealities, concentration scale, bulk magnetic susceptibility, NMR.

Introduction

The study of charge transfer complexes has attracted much attention over the years. These complexes have been examined by various experimental methods including vapour pressure osmometry [1, 2], conductometry [3], refractometry [4, 5] gas-liquid chromatography [6-9], ultraviolet visible (UV-Visible) spectroscopy [10-12], Infrared spectroscopy [13-14], fluorescence spectroscopy [15-17] and Nuclear Magnetic Resonance (NMR) [18-21]. Among this techniques NMR is particularly sensitive to small change in the electronic environment of a magnetic nucleus and therefore can be used in accurate measurement of charge transfer complexes' properties.

There are theoretical models presented to consider the behaviour of charge transfer complexes in particular those involved self-associations by hydrogen bonding [22-26].

Several equations have been suggested to evaluate formation constant K_{AD} for the charge transfer complex formation between electron acceptor (A) and electron donor (D) according to the following reaction: