

Electrochemical Studies on the Interaction of Cadmium Ion with Kryptofix 22 in MeOH-DMF Solutions at Different Temperatures

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Abstract The interaction between Cd²⁺ ion and Kryptofix 22 in pure MeOH and DMF solvents and their binary mixtures (0-100 % MeOH-DMF) at different temperatures (298.15-313.15) were measured by conductometric titrations. The conductance data in all cases were analysed using the Fuoss - Shedlovsky and Fuoss-Kraus methods to get the limiting molar conductance (Λ_0) and the association constant (K_A) simultaneously. Accordingly, the computer program of Fuoss equation has been used. The conductance studies indicate the formation of 1:1 complex between the Cd²⁺ ion and Kryptofix 22. From the conductivity data obtained, the values of the Walden products ($\Lambda_0\eta_0$) were also calculated. Based on the composition dependence of Walden products, the influence of the solvent composition on the solvation of the ion has been discussed. Thermodynamic parameters as well as refractive indices have been determined for Cd²⁺ ion in the mixed solvents at different temperatures with respect to solute-solvent interaction. This work gives a lot of data for cadmium ions which help in analysis.

Keywords Conductance, Cadmium Ion, Solvation, Association, Kryptofix-22, Thermodynamics of Solvation

1. Introduction

Macrocyclic polyether's were used recently for many applications on both scientific and applied fields in chemistry. The main goal of the present investigation is to study the interaction of some divalent metal ions i.e., Cd(NO₃)₂, with Kryptofix 22 in mixed solvent of methanol (MeOH) and dimethylformamide (DMF) at four temperatures (298.15, 303.15, 308.15 and 313.15 k). The interaction was studied electrochemically by the use of conductivity measurements. A lot of data on the association, dissociation and thermodynamic parameters of Cd(NO₃)₂ with Cryptand in MeOH-DMF mixtures were determined in order to facilitate the research for biologist in selecting the necessary ligand for getting rid of toxic salts found in the environment. Macrocyclic crown ethers have some applications in biological activity, industrial production, corrosion chemistry and phase transfer catalysis.

In complexation process, macrocycle ligands compete with solvent molecules towards the metal cations in solution. As a result, variation of the solvent can produce a significant change in the apparent binding properties of these ligands. Specifically, solvents of low dielectric constants and

solvating power lead to the greater complex stability than those tend to strong solvation of the metal cations. In addition, the selectivity for certain cations over others may be altered according to the reaction medium [1].

The experimental values of refractive indices for Cd(NO₃)₂ in mixed solvents, the excess refractive indices were calculated and their values show maximum solute-solvent interaction at about 80% MeOH percentage in the mixtures. Also, the electrical conductance data the association, dissociation and thermodynamic parameters for Cd(NO₃)₂ in presence and absence of Cryptand in mixed solvents (MeOH-DMF) at the above mentioned temperatures are calculated. The association and dissociation parameters are evaluated by using Fuoss-Shedlovsky method and their values are also supported with Fuoss-Kraus method. The computer program of Fuoss equation has been used. It was concluded that the association parameters for the salt used with Cryptand are generally increased by increasing the percentage of methanol in the mixed solvents.

2. Experimental

Methanol (MeOH, 99.8%), dimethylformamide (DMF, BDH, 99.8%) were used without further purification. The purity of the solvents was ascertained by comparing experimental values of densities and viscosities with those reported in the literature. Binary mixtures were prepared by mixing known volumes of each liquid in a stopper glass

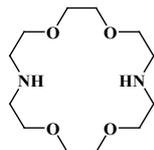
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bottle where the percentage by volume of the organic solvents varied from 0% to 100%. Both of the solvents were stored in sealed containers to prevent contamination with carbon dioxide and water from the air. Cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$, 99%), was provided from BDH. The salt was dried first in an oven at 100 °C and then stored in a desiccators over silica gel for at least 24 h. The kryptofix 22 used was provided from Fluka and used as received without any further purification. The structure of the Kryptofix 22 is given below.



Structure of Kryptofix 22 1,7,10,16-Tetraoxa-4,13-diazacyclooctadecane, $\text{C}_{12}\text{H}_{26}\text{N}_2\text{O}_4$; M. Wt. 262.35

The viscosity (η) of the pure solvents and binary mixtures over the entire range of composition and at the desired temperatures were measured using a calibrated U-type Ostwald viscometers immersed in a transparent glass-walled water bath having a thermal stability of $\pm 0.02\text{K}$. Then the absolute viscosity (η) was calculated by the following equation:

$$\eta = [(\rho t)/(\rho_0 t_0)] \eta_0 \quad (1)$$

Where ρ_1, ρ_0, t_1, t_0 and η_1, η_0 refer to the density, flow time, and viscosity of pure solvents or binary mixtures and water respectively (Table 1). The refractive indices (n_d) of pure solvents, binary mixtures and salt solutions at the desired temperatures were measured by an Abbe refractometer which was connected with ultra thermostat of the type (mgw Lauda cs-20) with accuracy to $\pm 0.01^\circ\text{C}$.

The dielectric constants (ϵ) of the pure solvents at different temperatures were taken by interpolation from the data in the literature [1], and dielectric constant for any solvent mixtures at the desired temperatures were calculated from the following equation:

$$\epsilon = x_{s(1)} \epsilon_{(1)} + x_{s(2)} \epsilon_{(2)} \quad (2)$$

Where $x_{s(1)}$ and $x_{s(2)}$ are the mole fraction by weight of the first and the second organic solvents, respectively; $\epsilon_{(1)}$ and $\epsilon_{(2)}$ are the dielectric constants of first and the second organic solvents in the binary organic-organic mixtures respectively. The results are shown in Table (2).

Conductance measurements were carried out with a standard digital direct reading conductivity meter of the type Jenway 4310 and a conductivity cell of cell constant 0.6 cm^{-1} . Also, some measurements were performed using a Beckman conductivity bridge model RE-18A in which the resistance of solution was determined in a jacketed glass cell permitting circulation of water in the jacket after connecting the cell with ultra thermostat of the type (mgw Luda S-20) and kept in a thermostat maintained at the desired temperature $\pm 0.01^\circ\text{C}$ for approximately 20 min, and then its specific conductivity or resistance was noted. These conductivity data is accurate and technical very good, easy and novel

method for cadmium ion determination.

3. Results and Discussion

The effects of $\text{Cd}(\text{NO}_3)_2$ concentrations on the molar conductance (Λ) in the absence and presence of Kryptofix 22 were extensively studied. Straight lines were obtained in the concentration range used at the different temperatures 298.15, 303.15, 308.15 and 313.15 K.

The limiting molar conductance (Λ_0) was obtained from the extrapolating the linear Onsager plots (Λ) versus ($C^{1/2}$) of $\text{Cd}(\text{NO}_3)_2$ to zero concentration [2]. The association constant (K_A) could be calculated by using two different methods of calculations, involving analysis of the experimental conductivity data (Λ) and (Λ_0) by using computer program. The two methods are:

3.1. Fuoss - Shedlovsky Method

In this method the values of association constant (K_A) were calculated by using the sets of the following equations from (3) to (10) [2-5]:

$$\frac{1}{\Lambda S_{(z)}} = \frac{1}{\Lambda_0} + \left(\frac{K_A}{\Lambda_0^2} \right) (C \cdot \Lambda \cdot \gamma_{\pm}^2 \cdot S_{(z)}) \quad (3)$$

$$S_{(z)} = \left[\frac{z}{2} + \left(1 + \left(\frac{z}{2} \right)^2 \right)^{1/2} \right]^2 \quad (4)$$

$$Z = S \cdot (\Lambda_0)^{-3/2} \cdot (C \Lambda)^{1/2} \quad (5)$$

$$S = a \cdot \Lambda_0 + b \quad (6)$$

$$a = 8.2 \times 10^5 (\epsilon T)^{1/2} \quad (7)$$

$$b = \frac{0.825}{\eta_0 (\epsilon T)^{1/2}} \quad (8)$$

$$\log \gamma_{\pm} = \frac{-A(\alpha C)^{1/2}}{\left[1 + B.r(\alpha C)^{1/2} \right]} \quad (9)$$

$$\alpha = \frac{\Lambda S_{(z)}}{\Lambda_0} \quad (10)$$

K_A is the association constant, (C) is the concentration of metal cation at the chosen points in the relation between (Λ) and, (γ_{\pm}) is the mean activity coefficients estimated from the Debye Hückel limiting law as modified by Robinson and Stockes, (ϵ) is the dielectric of the solvents, (η_0) is the viscosity of the solvents, (S) is the Onsager coefficient and finally (α) is the degree of dissociation^(6,7) (Tables 5-8).

The physical parameters like dielectric constant (ϵ) and viscosity (η_0) and refractive indices (n_d) for pure solvents and their mixtures at different temperatures which used in the analysis of the conductance data were taken from Tables (1)-(3).

3.2. Fuoss-Kraus Method

In this method the values of association constant (K_A) were recalculated by applying Fuoss-Kraus method [5] of calculation depending on Eq.5. The purpose was achieved by plotting the relation of $(1/\Lambda_0 \cdot S_{(z)})$ vs. $(C \Lambda \gamma_{\pm}^2 S_{(z)})$ which gave in all cases straight lines. Figures 1-2 represent the plots of $(1/\Lambda_0 \cdot S_{(z)})$ vs. $(C \Lambda \gamma_{\pm}^2 S_{(z)})$ from the Fuoss-Kraus method for

some metal complexes in all mixed solvents and at different temperatures.

Good agreement between the two above methods in association parameters is observed and the comparable results were tabulated in table (4). The conductance studies indicate 1:1 complex formation between the Cd^{2+} ion and Kryptofix. In most cases the association parameters of Cd^{2+} in absence and presence of Cryptand are greater in mixed solvents than in methanol. This is mainly due to the hydrogen bond strength in pure methanol which decreases in the mixed solvents and therefore facilitates the association of the cation.

It is concluded that the association constants generally increase by increasing the percentage of methanol in the mixed solvents (MeOH-DMF) due to the increase of association and decrease in the dissociation degree (α), dissociation constants (K_D) and the decrease in ion-ion interaction (activity coefficients γ) on the presence of different Cryptand compounds.

The degree of dissociation is almost constant in absence of Cryptand but a very large change (decreased) is observed on adding Cryptands to enhance and increase the association. The values of dissociation constant (K_D), the triple ion association constant (K_3)[2,6,7] were calculated and recorded in tables (5-12).

The Walden product values [2, 8] ($\Lambda_0\eta_0$) were calculated for $\text{Cd}(\text{NO}_3)_2$ in mixed mixtures of MeOH-DMF. The Walden product values as calculated from the limiting molar conductance values (Λ°) were informative from the point of view for ion-solvent interactions. The fluidity ratios (R_X) were also calculated and their values are given in Tables (5-12).

It was observed that R_X values were increased in the mixed solvents than in the pure MeOH or DMF solvents, this was an indication of selective solvation of the electrolyte. The decrease in the products of $\Lambda_0\eta_0$ indicates a strong solvent-solute interaction. As a result of that the solvent decrease the mobility of the ions. Activation Energies (E_a), Association Enthalpies (ΔH_A) and Association Entropies ($T\Delta S_A$) of $\text{Cd}(\text{NO}_3)_2$ solutions mixed (MeOH-DMF) were calculated, on plotting ($\log \Lambda_0$) values versus $1/T$ for $\text{Cd}(\text{NO}_3)_2$ in absence and presence of Cryptands straight lines were obtained. From their slopes[9] the E_a were evaluated and represented in Tables (13-14).

It was observed that the E_a values for $\text{Cd}(\text{NO}_3)_2$ in presence of Cryptand were greater than that in absence of Cryptand

Activation energies values are greater in the mixed sol-

vents than that of pure solvents due to mainly to solvent-solvent interactions. The values of Gibbs free energies of association (ΔG_A) of $\text{Cd}(\text{NO}_3)_2$ in mixed MeOH-DMF solvents were calculated from the association constant values by using Eq. 11.

$$\Delta G_A = -2.303RT \text{ Log } K_A \quad (11)$$

From the calculated ΔG_A values, the free energy of transfer (ΔG_T) from methanol (M) to the mixed MeOH-DMF (s) solvents was calculated. The values of ΔG_A and ΔG_T are also, reported in Tables (5-12) and in Figures (3-4). From the plots of logarithmic association constant values ($\text{Log } K_A$) of $\text{Cd}(\text{NO}_3)_2$ in absence and presence of Kryptofix 22 against the reciprocal values of the four temperatures 298.15, 303.15, 308.15 and 313.15K at the 1:1 (L:M)[10-12] ligand-metal ratio, straight lines were observed. From these straight relations shown in Figs. 3-4 the association enthalpies were calculated from their slopes (slope = $\Delta H_A/2.303RT$). The calculated ΔH_A values are tabulated in Tables (13-14). The entropies of association ($T\Delta S_A$) of $\text{Cd}(\text{NO}_3)_2$ were calculated by the use of Gibbs-Helmholtz equation:

$$\Delta G_A = \Delta H_A - T\Delta S_A \quad (12)$$

The calculated ΔS_A values are tabulated also in Tables (13-14). It is observed from these tables that the ΔH_A and ΔS_A values are increased with the increase of MeOH contents in the mixtures, which favour more association in the presence of methanol than in MeOH-DMF mixtures. Also, the enthalpies and entropies of $\text{Cd}(\text{NO}_3)_2$ association were increased by also adding Cryptand.

This order favours more association. From the thermodynamic parameters calculated, it was found that all these parameters are increased by increasing temperatures. This is due to the increase of interaction between Cd^{2+} and Cryptand by increasing temperature. The refractive indices of the mixed solvents (MeOH-DMF) and salt solutions of $\text{Cd}(\text{NO}_3)_2$ in mixed solvents at different temperatures (298.15, 303.15, 308.15 and 313.15K) were measured. And from the refractive indices (n_d) values, the excess refractive indices ($n_{d(E)}$) were calculated by applying eq.(13)[5-7,10-12]:

$$n_{d(E)} = n_{d(\text{mixed})} - [x_1 n_{d(1)} + x_2 n_{d(2)}] \quad (13)$$

Where (x_1) and (x_2) are the mole fraction of solvent 1 (MeOH) and solvent 2 (DMF) in their mixtures, (n_d) is the measured refractive indices of the mixed solvents or the salt solution. The values of (n_d) and ($n_{d(E)}$) of MeOH-DMF mixtures and the metal are given in Table (3). The excess refractive indices show maximum values at 80% MeOH-DMF percentages at all the used temperatures indicating maximum solute-solvent interactions at this percentage (Figure 5-6).

Table 1. The viscosities* (η_0) of MeOH-DMF mixtures at 298.15, 303.15, 308.15 and 313.15 K

Vol.% of MeOH	X_{MeOH}	MeOH-DMF mixtures			
		298.15K	303.15K	308.15K	313.15K
0	0.0000	0.8488	0.7588	0.7045	0.6566
20	0.3222	0.7698	0.7041	0.6494	0.6033
40	0.5590	0.7400	0.6734	0.6233	0.5738
60	0.7404	0.6392	0.6015	0.5526	0.5258
80	0.8838	0.6610	0.56997	0.5302	0.5133
100	1.0000	0.5759	0.5461	0.5309	0.4871

* (η_0) in poise

Table 2. The dielectric constants (ϵ) of MeOH-DMF mixtures at 298.15, 303.15, 308.15 and 313.15 K

Vol.% of MeOH	X_{MeOH}	MeOH-DMF			
		298.15 K	303.15 K	308.15 K	313.15 K
0	0.0000	38.6000	37.6000	36.2000	34.7000
20	0.3222	36.6990	35.7320	34.3641	32.9013
40	0.559	35.3019	34.3586	33.0143	31.5758
60	0.7404	34.2316	33.3063	31.9802	30.5588
80	0.8838	33.3856	32.4743	31.1626	29.7535
100	1.0000	32.7000	31.8000	30.5000	29.1000

Table 3. The refractive indices (n_d), the excess refractive indices ($n_{d(E)}$) and the molecular dipole polarizability* (α) of Cd(NO₃)₂ in MeOH-DMF mixtures at 298.15, 303.15, 308.15 and 313.15 K

Vol.% of MeOH	n_d				$n_{d(E)} \times 10^{-2}$				$\alpha \times 10^{-24}$			
	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
0	1.4280	1.4263	1.4248	1.4240	00.00	00.00	00.00	00.00	0.1020	0.1016	0.1011	0.1013
20	1.4112	1.4118	1.4110	1.4083	1.55	1.89	1.89	1.56	0.0984	0.0988	0.0984	0.0978
40	1.3940	1.3925	1.3920	1.3910	2.20	2.24	2.33	2.20	0.0948	0.0945	0.0944	0.0942
60	1.3783	1.3745	1.3730	1.3725	2.07	2.64	2.23	2.17	0.0906	0.0914	0.0903	0.0902
80	1.3575	1.3515	1.3500	1.3480	1.21	2.01	1.35	1.16	0.0856	0.0869	0.0853	0.0848
100	1.3278	1.3258	1.3250	1.3248	00.00	00.00	00.00	00.00	0.0803	0.0799	0.0797	0.0797

R in (mol.cm⁻³) and α (cm⁻³)

Table 4. Fuoss-Kraus association constant [Log K_A (F-K)] in comparison with Fuoss-Shedlovsky data [Log K_A (F-Sh)] for Cd(NO₃)₂ in presence of Kry-22 in mixed MeOH-DMF mixtures at 298.15, 303.15, 308.15 and 313.15K

Vol% of MeOH	298.15 K		303.15 K		308.15		313.15 K	
	Log K _A (F-K)	Log K _A (F-Sh)	Log K _A (F-K)	Log K _A (F-Sh)	Log K _A (F-K)	Log K _A (F-Sh)	Log K _A (F-K)	Log K _A (F-Sh)
0 %	3.170	4.14	3.203	4.44	4.71	4.56	3.17	3.82
20%	4.71	4.18	6.09	4.41	3.42	4.55	3.47	4.20
40%	4.17	3.32	4.34	4.91	6.06	4.29	5.67	4.35
60%	4.37	3.44	4.05	4.96	5.43	4.18	6.22	4.29
80%	4.35	3.42	3.60	4.90	5.01	4.12	7.09	4.28
100%	3.69	3.88	3.66	3.89	3.30	4.86	3.78	3.65

Table 5. The values of molar conductance* (Λ), limiting molar conductance* (Λ_0), degree of dissociation (α), activity coefficient (γ_{\pm}), association constant* (K_A), dissociation constant* (K_D), triple ion association constant* ($-K_3$), Gibbs free energy of association* (ΔG_A), transfer Gibbs free energy of association (ΔG_t), Walden product ($\Lambda_0\eta_0$) and the fluidity ratio (R_x) of Cd(NO₃)₂ in MeOH-DMF mixtures at 298.15K

Vol.% of MeOH	C	Λ	Λ_0	α	γ_{\pm}	K_A	K_D	K_3	ΔG_A	ΔG_t	$\Lambda_0\eta_0$	R_x
0	8 X 10 ⁻⁵	99.5	112	0.8996	0.9435	1.72X10 ³	5.81X10 ⁻⁴	1.07X10 ⁻³	-18.463	1.7669	0.9507	1.1634
20	8 X 10 ⁻⁵	83	94	0.8966	0.9393	1.80X10 ³	5.55X10 ⁻⁴	1.08X10 ⁻³	-18.575	1.6555	0.7236	0.8856
40	8 X 10 ⁻⁵	119.8	133	0.9130	0.9352	1.47X10 ³	6.78X10 ⁻⁴	0.99X10 ⁻³	-18.079	2.1513	0.9842	1.2045
60	8 X 10 ⁻⁵	127.5	148.15	0.8726	0.9338	2.37X10 ³	4.22X10 ⁻⁴	1.26X10 ⁻³	-19.255	0.9756	0.9470	1.1589
80	8 X 10 ⁻⁵	122.8	136	0.9165	0.9297	1.42X10 ³	7.04X10 ⁻⁴	0.97X10 ⁻³	-17.986	2.2443	0.8990	1.1002
100	8 X 10 ⁻⁵	116	141.88	0.8301	0.9309	3.51X10 ³	2.85X10 ⁻⁴	1.54X10 ⁻³	-20.230	0.0000	0.8171	1.0000

* C in (mol/l), Λ and Λ_0 in ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$), K_A and $-K_3$ in (mol/l), K_D in ($\text{mol}^{-1} \cdot \text{L}$) and ΔG_A and ΔG_t in (KJ/mol).

Table 6. The values of molar conductance* (Λ), limiting molar conductance* (Λ_0), degree of dissociation (α), activity coefficient (γ_{\pm}), association constant* (K_A), dissociation constant* (K_D), triple ion association constant* ($-K_3$), Gibbs free energy of association* (ΔG_A), transfer Gibbs free energy of association (ΔG_t), Walden product ($\Lambda_0\eta_0$) and the fluidity ratio (R_x) of Cd(NO₃)₂ in MeOH-DMF mixtures at 303.15K

Vol.% of MeOH	C	Λ	Λ_0	α	γ_{\pm}	K_A	K_D	K_3	ΔG_A	ΔG_t	$\Lambda_0\eta_0$	R_x
0	8 X 10 ⁻⁵	108	122	0.8966	0.9428	1.79X10 ³	5.60X10 ⁻⁴	1.09X10 ⁻³	-18.866	-0.2420	0.9257	1.1152
20	8 X 10 ⁻⁵	90.5	103	0.8922	0.9386	1.90X10 ³	5.27X10 ⁻⁴	1.12X10 ⁻³	-19.018	-0.3943	0.7252	0.8737
40	8 X 10 ⁻⁵	132	134.61	0.9952	0.9315	0.069X10 ³	145.58X10 ⁻⁴	0.19X10 ⁻³	-10.657	7.9670	0.9065	1.0921
60	8 X 10 ⁻⁵	139	156	0.9039	0.9316	1.67X10 ³	5.97X10 ⁻⁴	1.06X10 ⁻³	-18.703	-0.0793	0.9383	1.1304
80	8 X 10 ⁻⁵	128	144	0.9030	0.9290	1.70X10 ³	5.87X10 ⁻⁴	1.07X10 ⁻³	-18.745	-0.1211	0.8208	0.9888
100	8 X 10 ⁻⁵	135.7	152	0.9071	0.9267	1.62X10 ³	6.16X10 ⁻⁴	1.04X10 ⁻³	-18.624	0.0000	0.8301	1.0000

* C in (mol/l), Λ and Λ_0 in ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$), K_A and $-K_3$ in (mol/l), K_D in ($\text{mol}^{-1} \cdot \text{L}$) and ΔG_A and ΔG_t in (KJ/mol).

Table 7. The values of molar conductance* (Λ), limiting molar conductance* (Λ_0), degree of dissociation (α), activity coefficient (γ_{\pm}), association constant* (K_A), dissociation constant* (K_D), triple ion association constant* ($-K_3$), Gibbs free energy of association* (ΔG_A), transfer Gibbs free energy of association* (ΔG_t), Walden product ($\Lambda_0\eta_0$) and the fluidity ratio (R_x) of $\text{Cd}(\text{NO}_3)_2$ in MeOH-DMF mixtures at 308.15K

Vol.% of MeOH	C	Λ	Λ_0	α	γ_{\pm}	K_A	K_D	K_3	ΔG_A	ΔG_t	$\Lambda_0\eta_0$	R_x
0	8×10^{-5}	107.5	121	0.9007	0.9409	1.71×10^3	5.86×10^{-4}	1.06×10^{-3}	-19.063	-0.1135	0.8524	1.0849
20	8×10^{-5}	88.5	101	0.8909	0.9366	1.93×10^3	5.17×10^{-4}	1.13×10^{-3}	-19.381	-0.4319	0.6559	0.8348
40	8×10^{-5}	135	138.06	0.9932	0.9292	0.099×10^3	101.13×10^{-4}	0.23×10^{-3}	-11.766	7.1834	0.8605	1.0952
60	8×10^{-5}	141	157	0.9120	0.9288	1.52×10^3	6.60×10^{-4}	1.01×10^{-3}	-18.756	0.1931	0.8676	1.1042
80	8×10^{-5}	128	144	0.9039	0.9264	1.69×10^3	5.91×10^{-4}	1.06×10^{-3}	-19.039	-0.0896	0.7635	0.9717
100	8×10^{-5}	132	148	0.9070	0.9240	1.63×10^3	6.12×10^{-4}	1.04×10^{-3}	-18.949	0.0000	0.7857	1.0000

* C in (mol/l), Λ and Λ_0 in ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$), K_A and $-K_3$ in (mol/l), K_D in ($\text{mol}^{-1} \cdot \text{L}$) and ΔG_A and ΔG_t in (KJ/mol).**Table 8.** The values of molar conductance* (Λ), limiting molar conductance* (Λ_0), degree of dissociation (α), activity coefficient (γ_{\pm}), association constant* (K_A), dissociation constant* (K_D), triple ion association constant* ($-K_3$), Gibbs free energy of association* (ΔG_A), transfer Gibbs free energy of association* (ΔG_t), Walden product ($\Lambda_0\eta_0$) and the fluidity ratio (R_x) of $\text{Cd}(\text{NO}_3)_2$ in MeOH-DMF mixtures at 313.15K

Vol.% of MeOH	C	Λ	Λ_0	α	γ_{\pm}	K_A	K_D	K_3	ΔG_A	ΔG_t	$\Lambda_0\eta_0$	R_x
0	8×10^{-5}	109	130	0.8499	0.9403	2.90×10^3	3.45×10^{-4}	1.40×10^{-3}	-20.751	-0.2325	0.8536	1.1529
20	8×10^{-5}	91	109	0.8488	0.9355	2.96×10^3	3.38×10^{-4}	1.41×10^{-3}	-20.803	-0.2848	0.6576	0.8882
40	8×10^{-5}	119	140	0.8633	0.9310	2.61×10^3	3.83×10^{-4}	1.33×10^{-3}	-20.479	0.0387	0.8033	1.0850
60	8×10^{-5}	142	166.5	0.8660	0.9276	2.56×10^3	3.90×10^{-4}	1.32×10^{-3}	-20.430	0.0881	0.8755	1.1824
80	8×10^{-5}	126	149	0.8600	0.9250	2.73×10^3	3.66×10^{-4}	1.36×10^{-3}	-20.596	-0.0774	0.7648	1.0330
100	8×10^{-5}	129	152	0.8637	0.9224	2.65×10^3	3.77×10^{-4}	1.34×10^{-3}	-20.518	0.0000	0.7404	1.0000

* C in (mol/l), Λ and Λ_0 in ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$), K_A and $-K_3$ in (mol/l), K_D in ($\text{mol}^{-1} \cdot \text{L}$) and ΔG_A and ΔG_t in (KJ/mol).**Table 9.** The values of molar conductance* (Λ), limiting molar conductance* (Λ_0), degree of dissociation (α), activity coefficient (γ_{\pm}), association constant* (K_A), dissociation constant* (K_D), triple ion association constant* ($-K_3$), Gibbs free energy of association* (ΔG_A), transfer Gibbs free energy of association* (ΔG_t), Walden product ($\Lambda_0\eta_0$) and the fluidity ratio (R_x) of $\text{Cd}(\text{NO}_3)_2$ in the presence of Kryptofix-22 in MeOH-DMF mixtures at 298.15K

Vol.% of MeOH	C	Λ	Λ_0	α	γ_{\pm}	K_A	K_D	K_3	ΔG_A	ΔG_t	$\Lambda_0\eta_0$	R_x
0	8×10^{-5}	340	555.68	0.6154	0.9531	13.80×10^3	0.73×10^{-4}	3.14×10^{-3}	-23.621	-1.4707	4.7166	0.8759
20	8×10^{-5}	360	605	0.5987	0.9501	15.31×10^3	0.65×10^{-4}	3.31×10^{-3}	-23.879	-1.7280	4.6573	0.8649
40	8×10^{-5}	41.4	48	0.8846	0.9362	2.08×10^3	4.81×10^{-4}	1.13×10^{-3}	-18.930	3.2207	0.3552	0.0660
60	8×10^{-5}	67.6	80.5	0.8564	0.9344	2.77×10^3	3.61×10^{-4}	1.34×10^{-3}	-19.641	2.5097	0.5146	0.0956
80	8×10^{-5}	62	73.5	0.8613	0.9317	2.66×10^3	3.76×10^{-4}	1.31×10^{-3}	-19.540	2.6109	0.4858	0.0902
100	8×10^{-5}	668	935	0.7199	0.9355	7.62×10^3	1.31×10^{-4}	2.33×10^{-3}	-22.151	0.0000	5.3847	1.0000

* C in (mol/l), Λ and Λ_0 in ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$), K_A and $-K_3$ in (mol/l), K_D in ($\text{mol}^{-1} \cdot \text{L}$) and ΔG_A and ΔG_t in (KJ/mol).**Table 10.** The values of molar conductance* (Λ), limiting molar conductance* (Λ_0), degree of dissociation (α), activity coefficient (γ_{\pm}), association constant* (K_A), dissociation constant* (K_D), triple ion association constant* ($-K_3$), Gibbs free energy of association* (ΔG_A), transfer Gibbs free energy of association* (ΔG_t), Walden product ($\Lambda_0\eta_0$) and the fluidity ratio (R_x) of $\text{Cd}(\text{NO}_3)_2$ in the presence of Kryptofix-22 in MeOH-DMF mixtures at 303.15K

Vol.% of MeOH	C	Λ	Λ_0	α	γ_{\pm}	K_A	K_D	K_3	ΔG_A	ΔG_t	$\Lambda_0\eta_0$	R_x
0	8×10^{-5}	310	630	0.4947	0.9572	27.83×10^3	0.360×10^{-4}	4.47×10^{-3}	-25.785	-3.2321	4.7804	0.9313
20	8×10^{-5}	330	650	0.5106	0.9532	25.50×10^3	0.392×10^{-4}	4.28×10^{-3}	-25.565	-3.0124	4.5767	0.8916
40	8×10^{-5}	46	140	0.3313	0.9599	81.61×10^3	0.122×10^{-4}	7.54×10^{-3}	-28.496	-5.9431	0.9428	0.1837
60	8×10^{-5}	60	190	0.3182	0.9588	90.40×10^3	0.111×10^{-4}	7.99×10^{-3}	-28.754	-6.2010	1.1429	0.2226
80	8×10^{-5}	80	240	0.3358	0.9561	79.52×10^3	0.126×10^{-4}	7.51×10^{-3}	-28.431	-5.8778	1.3680	0.2665
100	8×10^{-5}	670	940	0.7184	0.9345	7.72×10^3	1.30×10^{-4}	2.35×10^{-3}	-22.553	0.0000	5.1333	1.0000

* C in (mol/l), Λ and Λ_0 in ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$), K_A and $-K_3$ in (mol/l), K_D in ($\text{mol}^{-1} \cdot \text{L}$) and ΔG_A and ΔG_t in (KJ/mol).

Table 11. The values of molar conductance* (Λ), limiting molar conductance* (Λ_0), degree of dissociation (α), activity coefficient (γ_{\pm}), association constant* (K_A), dissociation constant* (K_D), triple ion association constant* ($-K_3$), Gibbs free energy of association* (ΔG_A), transfer Gibbs free energy of association (ΔG_t), Walden product ($\Lambda_0\eta_0$) and the fluidity ratio (R_x) of $Cd(NO_3)_2$ in the presence of Kryptofix-22 in MeOH-DMF mixtures at 308.15K

Vol.% of MeOH	C	Λ	Λ_0	α	γ_{\pm}	K_A	K_D	K_3	ΔG_A	ΔG_t	$\Lambda_0\eta_0$	R_x
0	8×10^{-5}	270	600	0.4524	0.9577	36.01×10^3	0.278×10^{-4}	5.09×10^{-3}	-26.870	1.7656	4.2270	0.7511
20	8×10^{-5}	300	660	0.4571	0.9541	35.23×10^3	0.284×10^{-4}	5.03×10^{-3}	-26.814	1.8221	4.2860	0.7616
40	8×10^{-5}	45	82	0.5576	0.9464	19.61×10^3	0.509×10^{-4}	3.63×10^{-3}	-25.314	3.3225	0.5111	0.0908
60	8×10^{-5}	71	119	0.6054	0.9416	14.99×10^3	0.667×10^{-4}	3.21×10^{-3}	-24.626	4.0103	0.6576	0.1169
80	8×10^{-5}	65.5	106	0.6284	0.9383	13.20×10^3	0.758×10^{-4}	3.00×10^{-3}	-24.300	4.3361	0.5620	0.0999
100	8×10^{-5}	370	1060	0.3510	0.9520	71.75×10^3	0.139×10^{-4}	7.20×10^{-3}	-28.636	0.0000	5.6275	1.0000

* C in (mol/l), Λ and Λ_0 in ($\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$), K_A and $-K_3$ in (mol/l), K_D in ($mol^{-1} \cdot L$) and ΔG_A and ΔG_t in (KJ/mol).

Table 12. The values of molar conductance* (Λ), limiting molar conductance* (Λ_0), degree of dissociation (α), activity coefficient (γ_{\pm}), association constant* (K_A), dissociation constant* (K_D), triple ion association constant* ($-K_3$), Gibbs free energy of association* (ΔG_A), transfer Gibbs free energy of association (ΔG_t), Walden product ($\Lambda_0\eta_0$) and the fluidity ratio (R_x) of $Cd(NO_3)_2$ in the presence of Kryptofix-22 in MeOH-DMF mixtures at 313.15K

Vol.% of MeOH	C	Λ	Λ_0	α	γ_{\pm}	K_A	K_D	K_3	ΔG_A	ΔG_t	$\Lambda_0\eta_0$	R_x
0	8×10^{-5}	460	625.7	0.7404	0.9442	6.56×10^3	1.525×10^{-4}	2.157×10^{-3}	-22.874	-0.9840	4.1082	0.9694
20	8×10^{-5}	420	712.7	0.5933	0.9458	15.95×10^3	0.627×10^{-4}	3.379×10^{-3}	-25.187	-3.2969	4.2997	1.0146
40	8×10^{-5}	46	87	0.5374	0.9452	22.13×10^3	0.452×10^{-4}	3.868×10^{-3}	-26.039	-4.1500	0.4992	0.1178
60	8×10^{-5}	72.5	131	0.5613	0.9413	19.41×10^3	0.515×10^{-4}	3.663×10^{-3}	-25.698	-3.8080	0.6888	0.1625
80	8×10^{-5}	67	120	0.5670	0.9386	18.87×10^3	0.530×10^{-4}	3.605×10^{-3}	-25.625	-3.7350	0.6160	0.1454
100	8×10^{-5}	690	870	0.8004	0.9251	4.49×10^3	2.23×10^{-4}	1.783×10^{-3}	-21.889	0.0000	4.2378	1.0000

* C in (mol/l), Λ and Λ_0 in ($\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$), K_A and $-K_3$ in (mol/l), K_D in ($mol^{-1} \cdot L$) and ΔG_A and ΔG_t in (KJ/mol).

Table 13. The activation energy* (E_a), the enthalpy* (ΔH_A) and the entropy* (ΔS_A) changes of association of $Cd(NO_3)_2$ in MeOH-DMF mixtures at 298.15, 303.15, 308.15, 313.15K

Vol.% of first organic solvent	X_S (MeOH) by weight	E_a	ΔH_A	ΔS_A			
				289.15K	303.15K	308.15K	313.15K
0	0.000	6.8143	-28.4680	-0.0336	-0.0317	-0.0305	-0.0247
20	0.322	6.5929	-5.4732	0.0440	0.0447	0.0452	0.0490
40	0.559	2.7777	-29.6149	-0.0387	-0.0626	-0.0580	-0.0292
60	0.740	7.5235	-33.3505	-0.0473	-0.0483	-0.0474	-0.0413
80	0.884	4.2597	-34.3193	-0.0548	-0.0514	-0.0496	-0.0438
100	1.000	2.8129	-38.5662	-0.0615	-0.0658	-0.0637	-0.0577

* E_a , ΔG_A , ΔH_A in (KJ/mol) and ΔS_A in (KJ/K.mol).

Table 14. The enthalpy* (ΔH_A) and the entropy* (ΔS_A) changes of association of $Cd(NO_3)_2$ in the presence of Kryptofix-22 in MeOH-DMF mixtures at 298.15, 303.15, 308.15, 313.15K

Vol.% of first organic solvent	X_S (MeOH) by weight	E_a	ΔH_A	ΔS_A			
				289.15K	303.15K	308.15K	313.15K
0	0.000	4.807	-73.3910	-0.1670	-0.1571	-0.1510	-0.1614
20	0.322	7.858	-63.6738	-0.1335	0.1258	-0.1197	-0.1230
40	0.559	32.309	-129.8578	-0.3722	-0.3345	-0.3394	-0.3317
60	0.740	-25.895	-105.0316	-0.2865	-0.2517	-0.2611	-0.2535
80	0.884	25.747	-104.5779	-0.2854	-0.2513	-0.2606	-0.2522
100	1.000	9.528	-170.1760	-0.4967	-0.4872	-0.4595	-0.4738

* E_a , ΔH_A in (KJ/mol) and ΔS_A in (KJ/K.mol).

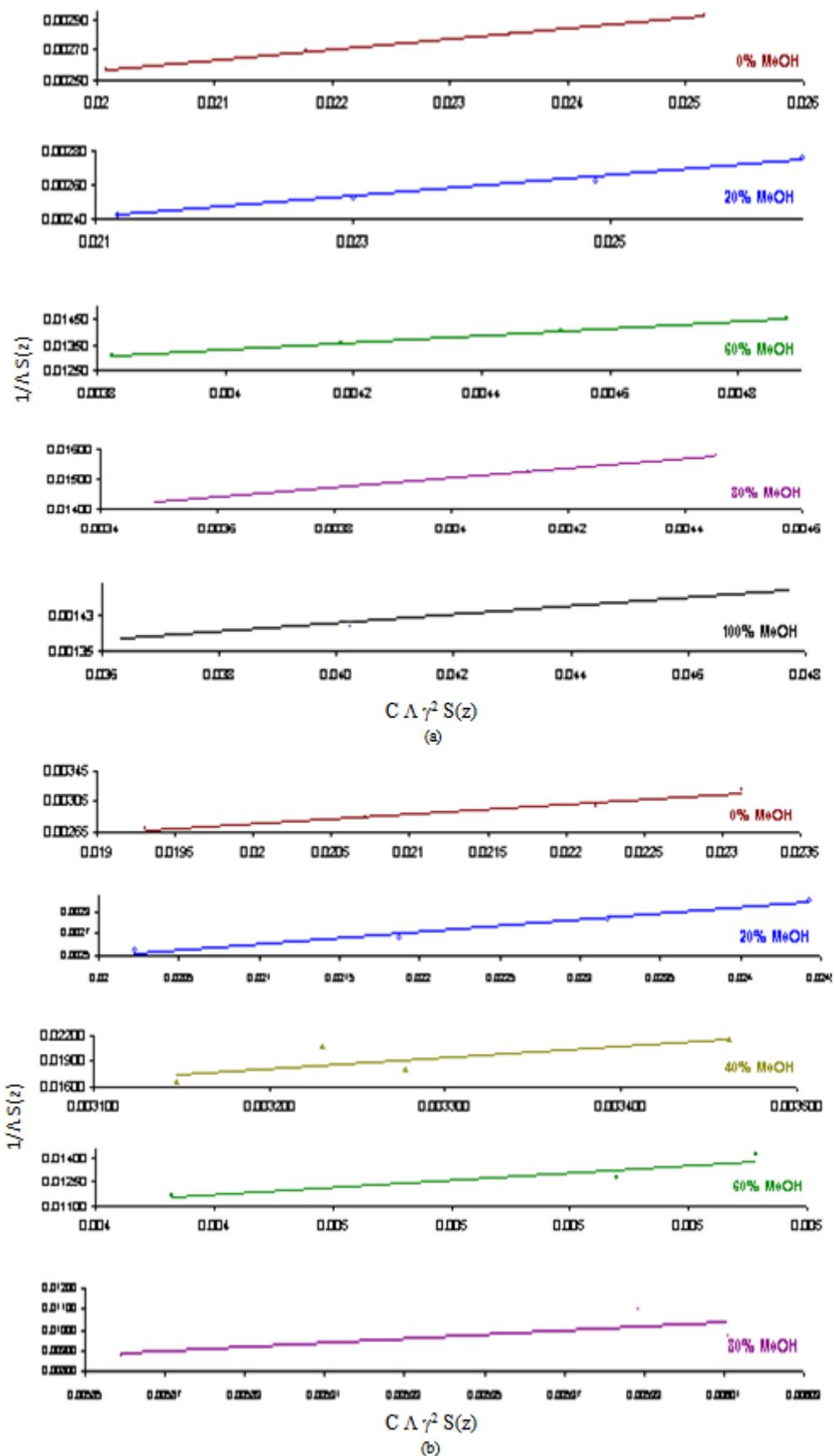


Figure 1. Fuoss-Kraus plots of $\text{Cd}(\text{NO}_3)_2$ in presence of Kry-22 in MeOH-DMF mixtures at (a) 298.15K and (b) 303.15K

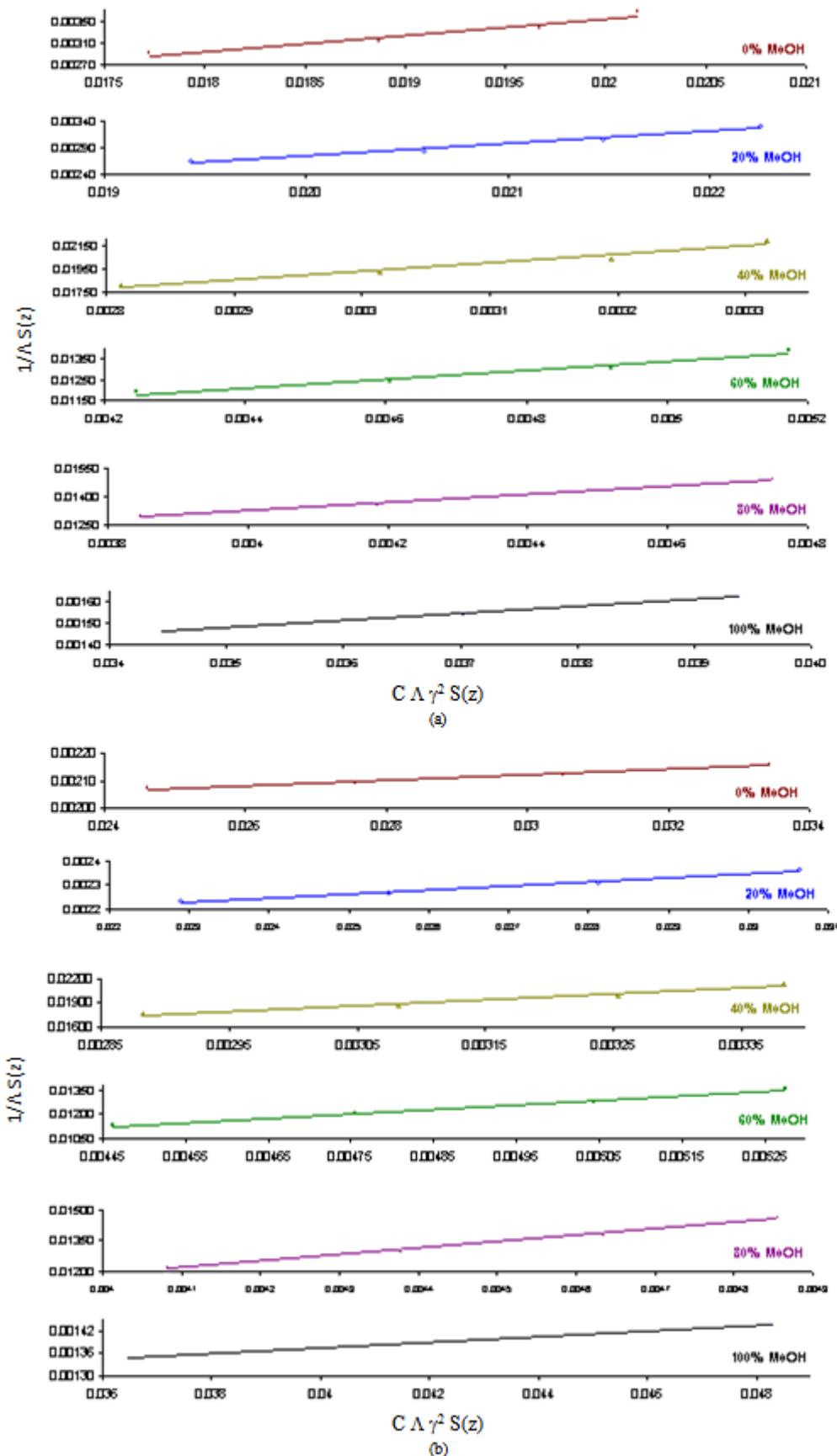


Figure 2. Fuoss-Kraus plots of $\text{Cd}(\text{NO}_3)_2$ in presence of Kry-22 in MeOH-DMF mixtures at (c) 308.15K and (d) 313.15K

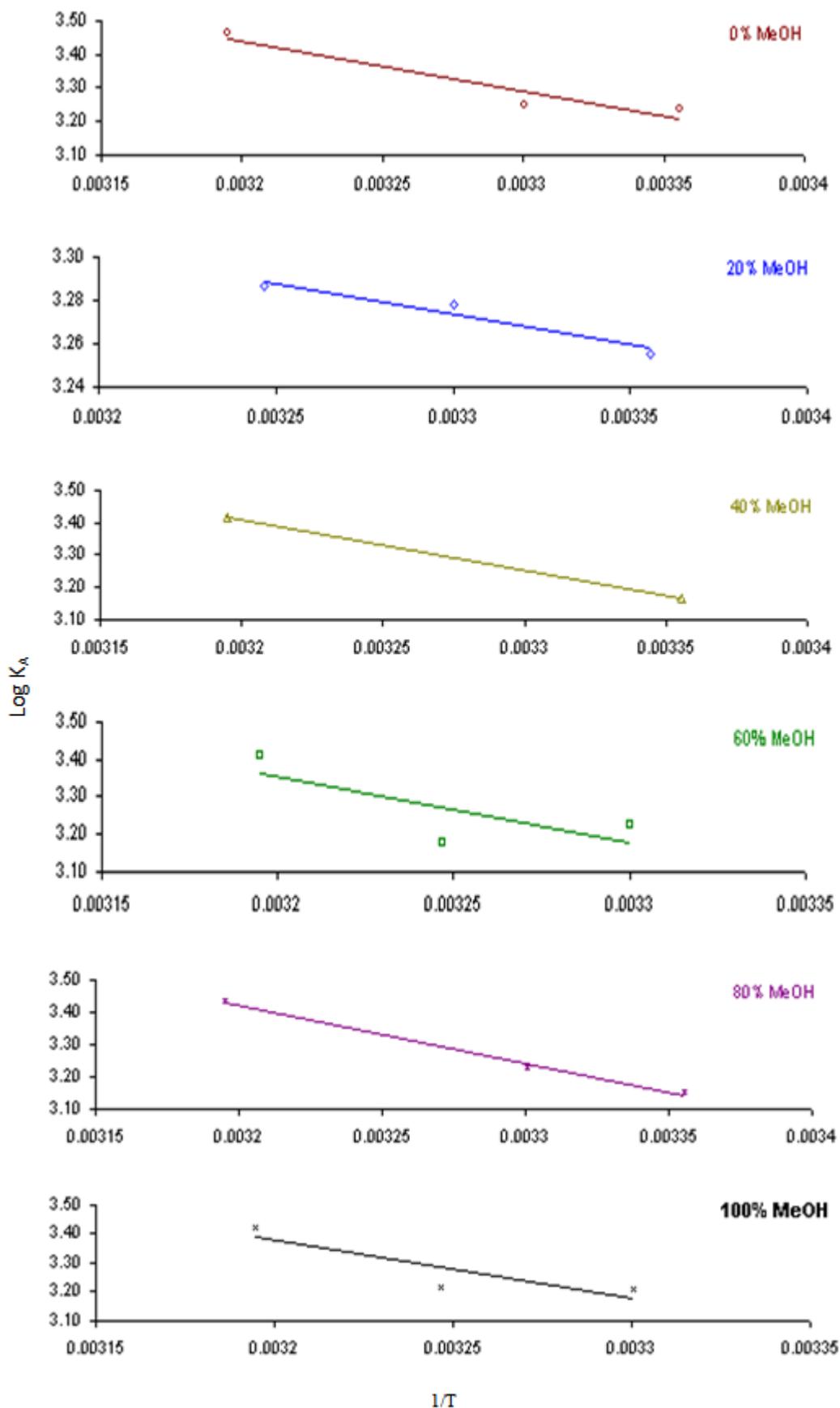


Figure 3. Variation of $\text{Log } K_A$ with $1/T$ in mixed MeOH-DMF solvents for $\text{Cd}(\text{NO}_3)_2$

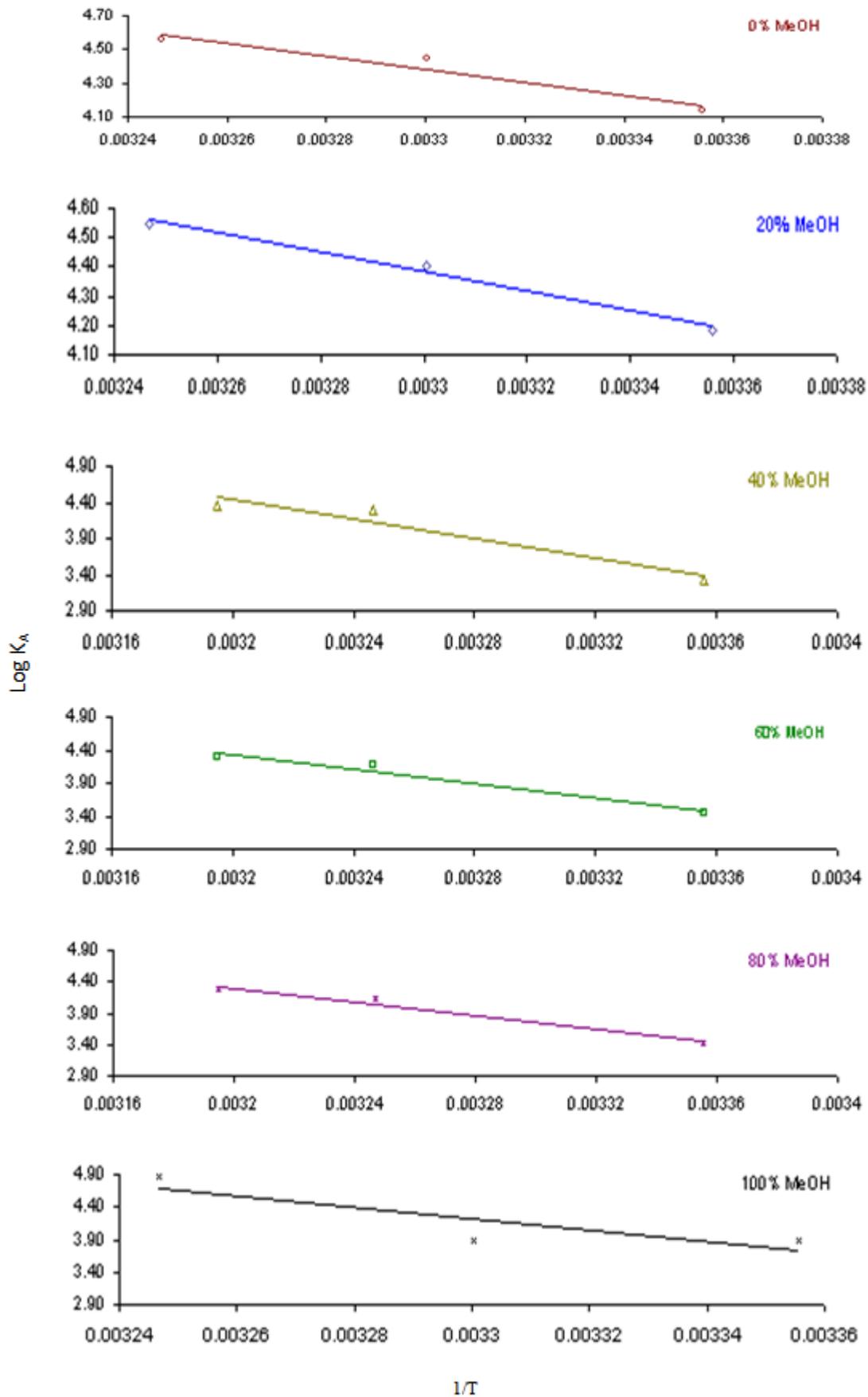


Figure 4. Variation of Log K_A with $1/T$ in mixed MeOH-DMF solvents for $Cd(NO_3)_2$ in presence of Kry-22

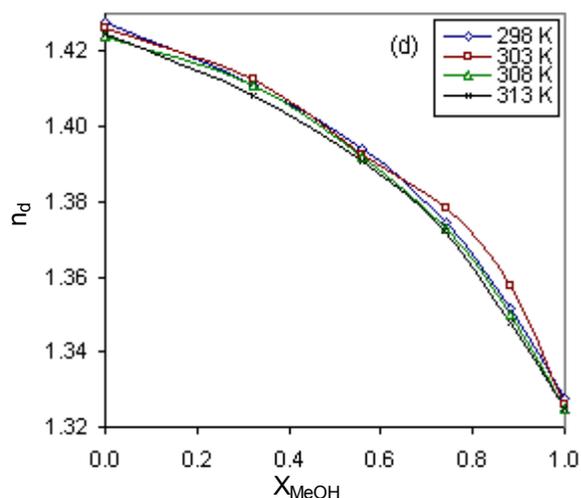


Figure 5. Variation of the refractive indices (n_d) with the mole fraction (X_{MeOH}) by weight of MeOH for $Cd(NO_3)_2$ at 298, 303, 308, 313 K in mixed MeOH-DMF solvents

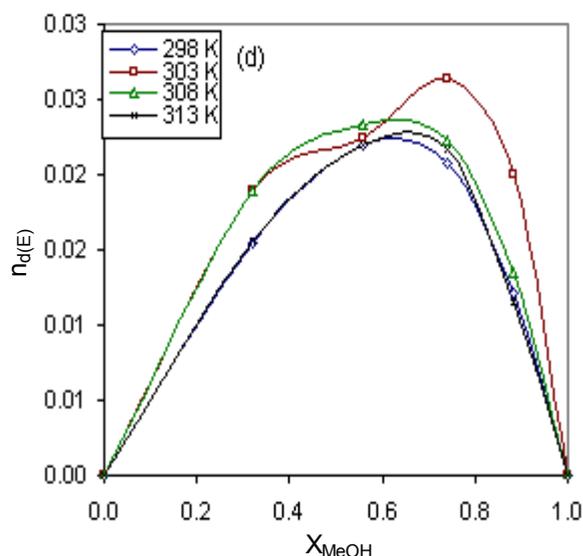


Figure 6. Variation of the excess refractive indices ($n_d(E)$) with the mole fraction (X_{MeOH}) by weight of MeOH for $Cd(NO_3)_2$ at 298, 303, 308, 313 K in mixed MeOH-DMF solvents

REFERENCES

- [1] E.A., Gomaa , *Thermochimica Acta*, 142 (1989) 19 and E. A. Gomaa , , *Croatica Chemica Acta*, 62 (1989) 475.
- [2] E.A.,Gomaa, M.A. ,Hafez, and M.N.H., Moussa, *Bull. Soc. Chim. Fr.*, 3 (1986)361.
- [3] E.A.Gomaa, *Thermochim. Acta*, 99, (1988)128.
- [4] M.A., Hafez, E. A. ,Gomaa, and M.N.H., Moussa, First conference of Chem. Faculty of science, Mansoura university, 24-26 Sep. (1986).
- [5] A. K., Covington and T.Dickinson,; "Physical Chemistry of Organic Solvent Systems", Plenum Press, London, (1973).
- [6] T. Shedlovsky, and R.L Kay, *J. Phys., Chem.*60(1956)151.
- [7] R.M. Fuoss, and F., Accascina, *Electrolytic conductance*, Interscience, New York (1959).
- [8] R.A., Robinson, and R. H. ,Stokes ; "Electrolyte Solutions", Wiley, P.463 (1968) New York.
- [9] P.,Walden; *Z.Phys. chem.*, 78(1912)257.
- [10] E. A. , Gomaa, *Thermochimica. Acta*, 152(1989)71.
- [11] E. A. Gomaa, *Thermochimica. Acta*, 156(1989)91.
- [12] A.A., EL-Khouly, E.A. ,Gomaa, and S., EL-Ashry, second conf. in Basic science, Assiut University, Assiut 2000.