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Investigating thermodynamic properties of the ternary systems of MCl (M = K, Rb, Cs) with aqueous mixed solvent: N,N-dimethylacetamide

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ABSTRACT

In this work, thermodynamic properties measurement for KCl/RbCl/CsCl in N,N-dimethylacetamide (DMA) (w) + H_2O ($1-w$) systems (where the $w = 0.10$, 0.20, 0.30) was carried out by potentiometric method using ion-selective electrodes at 298.15 K. Modeling of the activity coefficients of these ternary systems was based on the Pitzer, the modified Pitzer and the extended Debye–Hückel equations. Meanwhile, the osmotic coefficients, the standard free energy of transference from the water to the mixture have also been reported.

1. Introduction

There is a consensus that studying the thermodynamic properties of electrolyte in mixed organic + water solvents is very important which get a widely application in industrial and environmental, especially desalination and purification. Up to now, a lot of studies on the electrolyte in mixed water solvents have been reported by isopiestic method, potentiometric method and other measurements [1,2]. Potentiometric method has an advantage in the study of thermodynamic properties, such as rapidity, stability, simplicity and good selectivity. Many researches on thermodynamic properties of alkali metal halides in organic solvent have been determined using potentiometric method. For example, Lopes et al. investigated the activity coefficients of NaCl in ethanol + water mixtures [3]. Uspenskaya et al. determined the thermodynamic properties in the sodium chloride–water–1-butanol (iso-butanol) ternary systems [4]. The activity coefficients of NaBr in ethylene carbonate + water mixed solvents have been obtained by Hernández-Luis group [5]. Moreover, the thermodynamic property investigations of alkaline metal salts in some model compounds of proteins like amino acids, peptides as well as amide are of interest for researchers [6]. For instance, the activity coefficients determination of KCl in the KCl + formamide + water system by potentiometric measurement was studied by Ghalami-Choobar group [7]. Hernández-Luis et al. reported the activity coefficients of NaF/NaCl/NaBr + formamide + water [8–10] and NaCl + N-methylformamide + water systems [11]. Activity coefficients for NaCl in N,N-dimethylformamide + water mixed solvent have been investigated by the group of Alfredo Maestre [12]. As one of the amides, DMA is a highly polar solvent and also versatile solvent in various industrial processes [13]. However, the thermodynamic properties of electrolyte in DMA are not reported.

As an extension of our work on the thermodynamic properties of alkaline metal salts + organic solvent + water systems [14–17], this paper aims to investigate the ternary systems of MCl (M = K, Rb, Cs) + N,N-dimethylacetamide + water at 298.15 K. The experimental data were well fitted to the Pitzer, the modified Pitzer and the extended Debye–Hückel equations. The mean activity coefficients, osmotic coefficients, and the standard free energy of transference were also calculated herein.

2. Experimental

Potassium chloride (Sinopharm Chemical Reagent Co., Ltd, A.R. purity > 99.5%), rubidium chloride and cesium chloride (A.R. purity > 99.5%, Sichuan State Lithium Materials Co., Ltd.) were dried in vacuum at 393 K for the constant weight and then stockpiled in desiccators. DMA (Sinopharm Chemical Reagent Co., Ltd, A.R. purity > 99.5%), were used without pretreatment which contents very few water in original product could be ignored. Double distilled water was used in all experiments.

The ion-selective electrode (model 401) was obtained from Jiangsu Electroanalytic Instrument Factory. The K ion-selective electrode (ISE), Rb-ISE and Cs-ISE were filled with 0.1 mol·L^{-1} KCl solution, RbCl solution and CsCl solution relatively. Both the electrodes were of the type of PVC membrane and activated about 2 h before use. The membrane has no chemical reaction with DMA but dissolves in tetrahydrofuran.

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Table 1
Values of the molality m, potential E, mean activity coefficients $\gamma_\pm$ and osmotic coefficients Φ for KCl/RbCl/CsCl in pure water at 298.15 K.

m/mol·kg^{-1}	E/mV	$\gamma_\pm$	Φ	m/mol·kg^{-1}	E/mV	$\gamma_\pm$	Φ
KCl + pure water							
0.0020	−79.9	0.9520	0.9840	0.2471	152.2	0.6999	0.9092
0.0033	−53.8	0.9385	0.9796	0.2978	160.5	0.6859	0.9062
0.0078	−11.0	0.9105	0.9704	0.3818	171.8	0.6675	0.9028
0.0146	19.2	0.8840	0.9618	0.4606	180.4	0.6539	0.9006
0.0300	54.2	0.8460	0.9497	0.5507	188.6	0.6412	0.8989
0.0517	79.9	0.8125	0.9394	0.6657	197.0	0.6282	0.8978
0.0836	102.2	0.7799	0.9298	0.7735	203.7	0.6184	0.8974
0.1165	117.6	0.7561	0.9232	0.9975	214.7	0.6029	0.8980
0.1737	135.9	0.7264	0.9154				
RbCl + pure water							
0.0025	−169.6	0.9454	0.9818	0.1596	28.4	0.7240	0.9118
0.0060	−126.6	0.9195	0.9732	0.2107	40.9	0.7016	0.9057
0.0079	−113.3	0.9092	0.9698	0.2887	55.0	0.6759	0.8992
0.0152	−81.9	0.8805	0.9603	0.3705	65.9	0.6557	0.8945
0.0296	−49.8	0.8442	0.9485	0.4470	74.0	0.6407	0.8915
0.0495	−25.5	0.8114	0.9380	0.5488	82.9	0.6246	0.8886
0.0774	−4.6	0.7799	0.9282	0.6626	90.6	0.6103	0.8866
0.1066	9.9	0.7558	0.9209	0.7758	97.5	0.5987	0.8855
CsCl + pure water							
0.0015	−199.9	0.9568	0.9855	0.3889	62.7	0.6279	0.8781
0.0046	−144.5	0.9278	0.9758	0.4627	70.0	0.6118	0.8737
0.0076	−119.6	0.9095	0.9696	0.5500	77.7	0.5960	0.8697
0.0128	−94.4	0.8865	0.9619	0.6194	82.8	0.5853	0.8672
0.0223	−67.6	0.8573	0.9520	0.6855	87.2	0.5762	0.8652
0.0359	−45.1	0.8275	0.9419	0.7625	91.9	0.5669	0.8633
0.0539	−26.1	0.7989	0.9323	0.8236	95.3	0.5602	0.8621
0.1045	4.1	0.7465	0.9149	0.8832	98.3	0.5543	0.8611
0.1556	22.0	0.7120	0.9036	0.9400	101.1	0.5491	0.8604
0.2043	34.2	0.6874	0.8959	0.9930	103.3	0.5446	0.8598
0.3096	52.7	0.6491	0.8842				

Table 4
Values of E^0 and the Debye–Hückel parameters for KCl/RbCl/CsCl in the DMA + water mixtures at 298.15 K.

w	a/Å	c/kg·mol^{-1}	d/kg^2·mol^{-2}	E^0/mV	SD
KCl + DMA + water					
0.10	3.61	0.0510	−0.02216	259.1	0.24
0.20	5.18	−0.0389	0.01235	275.1	0.13
0.30	2.00	0.1296	−0.07364	300.9	0.34
RbCl + DMA + water					
0.10	5.53	−0.0927	0.02773	146.0	0.27
0.20	6.08	−0.0972	0.00972	168.1	0.14
0.30	6.92	−0.1922	0.04996	183.0	0.32
CsCl + DMA + water					
0.10	5.48	−0.1143	0.04992	147.2	0.27
0.20	1.61	0.1396	−0.04543	166.9	0.21
0.30	1.55	0.1331	−0.03543	185.9	0.29

Ag/AgCl electrode was conditioned overnight in 0.1 mol·L^{-1} HCl solution. Prior to the experiment, the electrodes were calibrated and presented a good Nernstian response. The potential readings were achieved on a pH/mV meter (Orion-868, America) and taken as the final readings when they became constant for at least 5 min. The uncertainty of the experimental of potential is ±0.1 mV.

BI-870 Dielectric Constant Meter (Brookhaven Instruments Corporation) was used to determine the relative permittivity of the mixed solvents at 298.15 ± 0.2 K. Calibration was performed under atmospheric pressure using double-distilled water ($D = 78.4$, 298.15 K). The density of the mixture has been measured by density meter (Anton Paar DMA 4500). The uncertainty of the experimental of relative permittivity and density is ±0.1 and ±0.00003 g·cm^{-3}.

3. Results

The cells used in this work belong to the type of cell without liquid junction with only one fluid, which as follows:

$$\mathrm{M-ISE|MCl}(m),\mathrm{water|Ag/AgCl} \tag{1}$$

$$\mathrm{M-ISE|MCl}(m),\mathrm{DMA}(w),\mathrm{water}(1-w)\mathrm{|Ag/AgCl} \tag{2}$$

where m stands for the molality of MCl (M = K, Rb, Cs) solution (between 0.0020 and 0.9975, 0.0025 and 0.7758, and 0.0015 and 0.9930,

Table 2
Values of average molecular mass M, dielectric constant D, density ρ, Debye–Hückel constants A, B and A_φ for DMA + water mixtures at 298.15 K.

w	M/g·mol^{-1}	D	ρ/g·cm^{-3}	A/kg$^{1/2}$·mol$^{-1/2}$	B/kg$^{1/2}$·mol$^{-1/2}$ Å^{-1}	A_φ/kg$^{1/2}$·mol$^{-1/2}$
DMA + water						
0.00	18.02	78.3	0.9970	0.5108	0.3286	0.3921
0.10	19.57	74.0	0.9957	0.5556	0.3378	0.4265
0.20	21.41	71.7	0.9962	0.5827	0.3433	0.4472
0.30	23.64	69.3	0.9973	0.6136	0.3494	0.4710

Table 3
Values of E^0, the Pitzer parameters and modified Pitzer parameters of KCl/RbCl/CsCl in DMA + water mixtures at 298.15 K.

w	Pitzer					Modified Pitzer				
	$\beta^{(0)}$/kg·mol^{-1}	$\beta^{(1)}$/kg·mol^{-1}	C^φ/kg^2·mol^{-2}	E^0/mV	SD	b/kg$^{1/2}$·mol$^{-1/2}$	B_{MX}/kg·mol^{-1}	C_{MX}/kg^2·mol^{-2}	E^0/mV	SD
KCl + DMA + water										
0.10	0.0820	0.2213	−0.03573	259.1	0.24	1.8023	0.0787	−0.0217	259.1	0.25
0.20	−0.0238	0.4966	0.02386	275.2	0.14	2.7988	−0.0252	0.0035	275.0	0.13
0.30	0.1477	−0.0801	−0.11809	300.9	0.35	0.9646	0.1658	−0.0607	300.9	0.34
RbCl + DMA + water										
0.10	−0.0859	0.5034	0.04727	146.1	0.28	2.9766	−0.0884	0.0158	145.9	0.27
0.20	−0.1010	0.6321	0.02507	168.3	0.15	3.3740	−0.0939	0.0018	168.0	0.14
0.30	−0.2368	0.8269	0.10327	183.2	0.35	3.9334	−0.2005	0.0303	182.9	0.31
CsCl + DMA + water										
0.10	−0.1065	0.4913	0.07790	147.3	0.29	2.8790	−0.1087	0.0314	147.2	0.25
0.20	0.1354	−0.1498	−0.06959	166.9	0.21	0.7725	0.1676	−0.0365	166.9	0.21
0.30	0.1226	−0.1608	−0.05337	185.9	0.29	0.7619	0.1580	−0.0286	185.9	0.29