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# Density and viscosity of aqueous solution of $K_2CrO_4$/KOH mixed electrolytes

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**Abstract:** The physicochemical properties are very important in theoretical investigation of aqueous electrolyte solution and industrial design of hydrometallurgical processes. In the green hydrometallurgical process of chromite ore with sub-molten salt medium of KOH, the ternary system of $KOH+K_2CrO_4+H_2O$ is essential to process control and industrial operation. In order to satisfy the needs of both fundamental research and industrial application, the dynamic viscosity ($\eta$) and density ($\rho$) of mixed aqueous electrolyte solution of KOH and $K_2CrO_4$ were measured over a temperature range from 15 to 60 ℃ by using Ubbelohde-type capillary viscometers and a series of densimeters, respectively. The temperature is controlled to an accuracy of ±0.01 ℃ throughout the experiment with thermostat. The dynamic viscosity and density of the ternary systems are performed as functions of chromate and hydroxide concentration and temperature. The regression equations for viscosity and density are obtained with a least-square method and the calculated values are consistent well with the experimental data. The semi-empirical equation obtained will be helpful and instructive to industrial application.

**Key words:** viscosity; density; potassium chromate; potassium hydroxide; mixed electrolytes

## 1 Introduction

The green hydrometallurgical process of chromite ore with sub-molten salt medium is proposed and developed to solve the serious environmental problem in the traditional production process of chromate[1−2]. In the green process, the efficient separation of $K_2CrO_4$ from the multi-component electrolytes system of $K_2CrO_4$-KOH-$KAlO_2$-$K_2SiO_3$-$K_2MnO_4$-$H_2O$ is very important[2−5]. As for both fundamental research and industrial application, the needs for physicochemical property of the multiple-solute electrolyte solution become imperative and urgent. The ternary system of $KOH+K_2CrO_4+H_2O$ studied in this work is one of the sub-systems of the mixed electrolytes. However, to the authors' knowledge, the physicochemical property data of this ternary aqueous electrolyte have seldom been reported so far.

The density is one of the key thermodynamic properties of electrolyte solutions and belongs to an equilibrium property, while the viscosity is one of the key transport properties of electrolyte solutions and belongs to a dynamic state property. Both of them are indispensable basic data to engineering design and process optimization[6−8]. In the present work, the dynamic viscosity ($\eta$) and density ($\rho$) of the ternary system of $KOH+K_2CrO_4+H_2O$ were measured and the experimental data as a function of chromate and hydroxide concentration over the temperature range from 15 to 60 ℃ were regressed. A semi-empirical equation describing the relationship between the viscosity or density of the solutions as well as the primary variables was obtained.

## 2 Experimental

### 2.1 Apparatus and reagents

The main apparatus used in this work included a thermostat (type JWC-32$C_1$, Shanghai S.R.D Scientific Instrument Co. Ltd.) with a constant water circulation for maintaining constant temperature throughout the

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experiment to an accuracy of ±0.01 ℃, an electronic analytical balance (Mettler AE240) with an uncertainty of 0.1 mg, an electronic digital stopwatch correct to ±0.01 s, a series of densimeters with an accuracy up to 0.1 mg/cm$^3$ and Ubbelohde capillary viscometer (type 1836-A, Shanghai Liangjing Glass Instruments Factory, China) with a diameter of 0.46 mm.

The chemical reagents potassium chromate ($K_2CrO_4$) and potassium hydroxide (KOH) used in this work were AR grade and GR grade, respectively, and used directly without further purification (potassium chromate, AR, ≥98.5% (mass fraction); potassium hydroxide, GR, ≥85.0% (mass fraction)). The pure water used throughout the experiments was double-distilled and its conductivity was lower than 0.1 mS/m.

The solutions consisting of individual samples with total volume of 1 L were prepared on the basis of mass, using the analytical balance. The chromate and hydroxide concentration were determined by titration with $(NH_4)_2Fe(SO_4)_2$ and HCl standard solution in the presence of indicator of *n*-phenylanthranilic acid and phenolphthalain, respectively.

### 2.2 Density measurement

The density measurements were carried out by a series of densimeters. A suitable densimeter was selected and then immersed in the solution. After the solution temperature reached a desired point, the density value was read from the meniscus of the solution with the densimeter.

### 2.3 Viscosity measurement

The viscosity ($\eta$) was measured using a Ubbelohde capillary viscometer, which was placed inside the thermostat. The viscometer was calibrated with high-purity water at 15, 25, 30, 40, 50 and 60 ℃, and was thoroughly cleaned and perfectly dried, then filled with experimental solutions. After thermal equilibrium had been achieved at the required temperature, the times of the flow of the solutions and water were recorded with the electronic digital stopwatch. At least five repetitions of each datum point obtained were reproducible to ±0.05 s for solutions and ±0.02 s for water, and the results were averaged. The viscosity ($\eta$) was then calculated according to Eq.(1)[7−8]

$$\frac{\eta}{\eta_w}=\frac{\rho}{\rho_w}\frac{t}{t_w} \qquad (1)$$

where $\eta$ (mPa·s), $\rho$ (g·cm$^{-3}$), $t$ (s), $\eta_w$ (mPa·s), $\rho_w$ (g·cm$^{-3}$), $t_w$ (s) represent the viscosity, density and flow time of the mixture and water, respectively. The densities and viscosities of pure water were taken from Data Book of Chemistry & Chemical Industry Physical Properties (Inorganic compounds)[9].

In order to improve the accuracy, $t_w$ was determined daily before and after the test solution measurements[10]. From several hundred independent runs, the results show that the efflux times for water drop over a period of about five months. This variation is consistent with a very slow dissolution of the glass in the caustic solutions causing a small but noticeably increase in the capillary bore. This dissolution is sufficiently slow and has no practical effect on the measured viscosity.

## 3 Results and discussion

The experimental densities and viscosities for $KOH+K_2CrO_4+H_2O$ ternary system at the temperatures of 15, 25, 30, 40, 50 and 60 ℃ are listed in Table 1. From Table 1, the densities decrease with increasing temperature at fixed chromate and hydroxide concentration and increase with increasing chromate or hydroxide concentration at constant temperature. The density variation is due to the expansion of the volume of the solution with the increasing temperature of the system. The same occurs at the viscosities of the system. This results show that strong interactions between the solute species and water molecules exist in the solution and that this interaction weakens with increasing temperature.

### 3.1 Correlation of densities

The effects of temperature and concentration on densities are shown in Figs.1 and 2. As can be seen, the mixture densities display satisfactorily linear dependence (with $R^2 > 0.995$) on temperature and solute concentration.

According to this law, the experimental data were regressed by Matlab 6.5 with the least-squares method[11−15]. The regression equation describing the relationship between the solution densities and basic variables (temperature, chromate and hydroxide concentration) is

$$\rho=1.019\,8-4\times10^{-4}\theta+0.043\,5c(\text{KOH})+0.128\,3c(\text{K}_2\text{CrO}_4) \qquad (2)$$

where $\rho$ (g/cm$^3$), $\theta$ (℃), $c$(KOH) (mol/L) and $c(K_2CrO_4)$ (mol/L) represent the density, temperature, chromate and hydroxide concentration in terms of molality of the solution, respectively.

Some of the calculated values and relative errors are listed in Table 2. This semi-empirical equation enables to predict the densities of $KOH+K_2CrO_4+H_2O$ ternary system over the ranges of 15 ℃≤$\theta$≤60 ℃, 0.5 mol/L≤$c$(KOH)≤3 mol/L and 0≤$c(K_2CrO_4)$<Saturation, with average error of 0.3410% and a maximum error of 1.3159% under conditions of $\theta$=60 ℃, $c$(KOH)=1.012 1

**Table 1** Experimental densities ($\rho$) and viscosities ($\eta$) of ternary system ($KOH+K_2CrO_4+H_2O$) as a function of chromate and hydroxide concentration from 15 ℃ to 60 ℃

| $c(KOH)$/ ($mol\cdot L^{-1}$) | $c(K_2CrO_4)$/ ($mol\cdot L^{-1}$) | $\rho/(g\cdot cm^{-3})$ | | | | | | $\eta$/(mPa·s) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 15 ℃ | 25 ℃ | 30 ℃ | 40 ℃ | 50 ℃ | 60 ℃ | 15 ℃ | 25 ℃ | 30 ℃ | 40 ℃ | 50 ℃ | 60 ℃ |
| 0.507 6 | 0 | 1.025 7 | 1.023 9 | 1.022 1 | 1.018 3 | 1.014 9 | 1.010 9 | 1.204 2 | 0.948 2 | 0.852 1 | 0.702 1 | 0.590 9 | 0.505 7 |
| 0.498 5 | 0.197 5 | 1.058 5 | 1.056 8 | 1.054 4 | 1.049 5 | 1.044 6 | 1.038 8 | 1.233 8 | 0.988 3 | 0.891 0 | 0.735 4 | 0.619 9 | 0.532 5 |
| 0.501 8 | 0.500 5 | 1.099 9 | 1.097 2 | 1.095 8 | 1.092 2 | 1.087 6 | 1.082 8 | 1.306 2 | 1.049 5 | 0.946 3 | 0.786 6 | 0.667 0 | 0.573 8 |
| 0.503 1 | 0.999 0 | 1.170 2 | 1.166 9 | 1.165 2 | 1.161 8 | 1.156 7 | 1.151 5 | 1.452 7 | 1.168 3 | 1.060 9 | 0.889 0 | 0.753 3 | 0.653 3 |
| 0.502 0 | 2.072 9 | 1.296 3 | 1.292 3 | 1.290 2 | 1.284 1 | 1.279 8 | 1.274 5 | 1.826 2 | 1.481 0 | 1.346 6 | 1.132 3 | 0.970 2 | 0.841 6 |
| 0.503 3 | 2.247 0 | 1.337 4 | 1.333 2 | 1.330 9 | 1.325 1 | 1.321 5 | 1.316 2 | 1.963 4 | 1.601 5 | 1.467 5 | 1.225 1 | 1.049 2 | 0.925 4 |
| 0.995 2 | 0 | 1.050 9 | 1.047 9 | 1.046 8 | 1.043 2 | 1.038 6 | 1.033 9 | 1.267 0 | 1.005 1 | 0.905 7 | 0.749 3 | 0.631 2 | 0.540 5 |
| 0.997 4 | 0.208 6 | 1.080 4 | 1.077 2 | 1.076 1 | 1.072 4 | 1.068 2 | 1.063 4 | 1.315 2 | 1.051 6 | 0.947 3 | 0.785 1 | 0.663 6 | 0.570 1 |
| 0.998 5 | 0.517 4 | 1.124 9 | 1.121 5 | 1.120 1 | 1.116 3 | 1.111 1 | 1.106 9 | 1.393 4 | 1.123 8 | 1.017 5 | 0.846 6 | 0.718 1 | 0.618 6 |
| 0.997 4 | 1.068 6 | 1.195 0 | 1.191 2 | 1.189 9 | 1.185 6 | 1.181 4 | 1.176 7 | 1.579 5 | 1.279 8 | 1.163 0 | 0.974 0 | 0.830 3 | 0.719 4 |
| 0.998 6 | 1.658 3 | 1.260 3 | 1.257 1 | 1.255 2 | 1.251 2 | 1.247 0 | 1.242 2 | 1.749 5 | 1.421 7 | 1.293 7 | 1.087 2 | 0.928 7 | 0.835 4 |
| 1.012 1 | 2.107 7 | 1.311 1 | 1.307 2 | 1.305 2 | 1.301 8 | 1.296 4 | 1.291 9 | 1.921 2 | 1.571 3 | 1.440 7 | 1.209 6 | 1.037 3 | 0.902 0 |
| 1.497 1 | 0 | 1.073 3 | 1.071 1 | 1.068 6 | 1.065 8 | 1.060 2 | 1.055 9 | 1.336 2 | 1.067 8 | 0.962 2 | 0.798 7 | 0.672 3 | 0.576 6 |
| 1.503 9 | 0.199 1 | 1.105 4 | 1.100 4 | 1.098 8 | 1.094 5 | 1.090 0 | 1.085 5 | 1.392 3 | 1.113 0 | 1.006 2 | 0.836 4 | 0.707 3 | 0.608 1 |
| 1.499 3 | 0.504 4 | 1.148 0 | 1.145 2 | 1.142 9 | 1.138 2 | 1.133 8 | 1.129 3 | 1.476 4 | 1.193 4 | 1.083 0 | 0.899 6 | 0.806 4 | 0.703 7 |
| 1.500 5 | 1.024 0 | 1.212 1 | 1.209 2 | 1.208 1 | 1.204 2 | 1.198 1 | 1.194 5 | 1.637 9 | 1.327 2 | 1.204 5 | 1.009 2 | 0.857 9 | 0.741 9 |
| 1.507 3 | 1.594 3 | 1.281 1 | 1.276 3 | 1.274 6 | 1.270 1 | 1.266 3 | 1.262 0 | 1.877 7 | 1.524 6 | 1.385 0 | 1.162 4 | 0.992 2 | 0.859 7 |
| 1.508 4 | 1.788 1 | 1.322 0 | 1.316 2 | 1.314 5 | 1.310 1 | 1.305 3 | 1.301 2 | 2.098 2 | 1.704 9 | 1.534 9 | 1.325 5 | 1.098 0 | 0.945 9 |
| 1.999 9 | 0 | 1.097 5 | 1.094 4 | 1.092 8 | 1.088 6 | 1.083 9 | 1.079 3 | 1.418 1 | 1.137 1 | 1.026 7 | 0.852 4 | 0.719 6 | 0.618 4 |
| 1.997 6 | 0.205 1 | 1.126 1 | 1.122 9 | 1.120 8 | 1.116 9 | 1.113 7 | 1.108 8 | 1.477 0 | 1.186 0 | 1.073 3 | 0.891 8 | 0.757 1 | 0.651 3 |
| 1.999 8 | 0.490 8 | 1.167 4 | 1.163 2 | 1.162 1 | 1.157 5 | 1.154 0 | 1.149 2 | 1.574 7 | 1.270 2 | 1.151 0 | 0.958 6 | 0.817 5 | 0.703 9 |
| 2.004 4 | 1.008 7 | 1.235 0 | 1.230 2 | 1.228 3 | 1.225 1 | 1.218 7 | 1.214 4 | 1.777 2 | 1.437 2 | 1.305 0 | 1.092 1 | 0.928 3 | 0.802 1 |
| 1.999 9 | 1.218 2 | 1.260 3 | 1.255 5 | 1.254 0 | 1.249 4 | 1.245 0 | 1.239 7 | 1.874 9 | 1.517 4 | 1.378 2 | 1.153 4 | 0.982 6 | 0.849 1 |
| 1.999 9 | 1.483 8 | 1.292 8 | 1.288 6 | 1.286 1 | 1.281 2 | 1.276 1 | 1.271 5 | 1.994 8 | 1.617 2 | 1.467 6 | 1.230 3 | 1.048 5 | 0.907 0 |
| 2.497 0 | 0 | 1.120 0 | 1.116 8 | 1.114 8 | 1.110 1 | 1.106 0 | 1.103 1 | 1.506 8 | 1.210 1 | 1.094 1 | 0.908 0 | 0.767 6 | 0.660 3 |
| 2.497 0 | 0.203 3 | 1.147 5 | 1.143 9 | 1.141 4 | 1.137 5 | 1.133 0 | 1.128 2 | 1.575 2 | 1.268 9 | 1.146 9 | 0.953 9 | 0.808 7 | 0.696 0 |
| 2.501 5 | 0.501 1 | 1.187 0 | 1.183 0 | 1.180 3 | 1.176 2 | 1.172 1 | 1.167 2 | 1.681 3 | 1.356 4 | 1.229 7 | 1.024 9 | 0.871 4 | 0.750 5 |
| 2.497 0 | 0.800 0 | 1.225 9 | 1.222 1 | 1.220 6 | 1.216 4 | 1.211 7 | 1.206 2 | 1.793 5 | 1.448 4 | 1.314 3 | 1.097 0 | 0.932 6 | 0.803 3 |
| 2.497 0 | 1.025 4 | 1.249 2 | 1.245 0 | 1.243 4 | 1.239 0 | 1.234 1 | 1.229 0 | 1.878 6 | 1.517 9 | 1.377 8 | 1.150 9 | 0.979 0 | 0.845 2 |
| 2.501 5 | 1.199 3 | 1.272 0 | 1.267 9 | 1.266 0 | 1.261 9 | 1.257 0 | 1.251 9 | 1.971 9 | 1.594 2 | 1.435 5 | 1.209 1 | 1.029 7 | 0.889 5 |
| 3.000 9 | 0 | 1.147 2 | 1.144 1 | 1.141 9 | 1.137 8 | 1.133 7 | 1.128 2 | 1.622 5 | 1.303 6 | 1.179 6 | 0.980 1 | 0.829 4 | 0.711 9 |
| 3.007 8 | 0.199 6 | 1.172 9 | 1.171 0 | 1.167 2 | 1.163 3 | 1.159 0 | 1.154 0 | 1.693 7 | 1.364 1 | 1.233 2 | 1.026 9 | 0.871 2 | 0.748 5 |
| 3.000 9 | 0.497 5 | 1.207 0 | 1.203 0 | 1.201 0 | 1.196 8 | 1.193 0 | 1.187 5 | 1.787 6 | 1.441 9 | 1.306 1 | 1.136 8 | 0.924 8 | 0.796 5 |
| 3.000 9 | 0.808 7 | 1.243 8 | 1.240 7 | 1.239 8 | 1.235 0 | 1.230 2 | 1.225 1 | 1.923 0 | 1.597 1 | 1.444 8 | 1.202 6 | 0.996 6 | 0.857 8 |
| 3.007 8 | 0.993 5 | 1.266 1 | 1.261 8 | 1.261 1 | 1.256 8 | 1.252 8 | 1.247 0 | 2.007 0 | 1.168 2 | 1.469 7 | 1.227 0 | 1.043 9 | 0.899 4 |

mol/L and $c(K_2CrO_4)$ = 2.107 7 mol/L.

### 3.2 Correlation of viscosities

The effects of the three independent variables on mixture viscosity were investigated using the nonlinear regression method in Origin 8.0. The results show that the nature logarithm of the mixture viscosity display satisfactorily linear dependence ($R^2$>0.995) on chromate and hydroxide concentration, and the curves of dynamic viscosity vs temperature accord with second-order polynomial equations ($R^2$>0.999) (see Figs.3 and 4).

The regression equation for viscosity obtained by the least-squares method[11−13, 15] is

$$\eta=\exp[0.430\,0-0.025\,1\theta+1\times10^{-4}\theta^2+0.130\,7c(KOH)+0.236\,6c(K_2CrO_4)] \quad (3)$$

where $\eta$ (mPa·s) represents the viscosity of the solution.

Some of the calculated viscosity values are presented in Table 2. The average error between the calculated and the experimental data is 1.1447% with a maximum of

**Table 2** Comparison of experimental densities and viscosities of $KOH+K_2CrO_4+H_2O$ with calculated data

| $\theta$/°C | $c$(KOH)/ $(mol\cdot L^{-1})$ | $c(K_2CrO_4)$/ $(mol\cdot L^{-1})$ | $\rho/(g\cdot cm^{-3})$ | | Relative error/% | $\eta$/(mPa·s) | | Relative error/% |
|---|---|---|---|---|---|---|---|---|
| | | | Exp. | Cal. | | Exp. | Cal. | |
| 15 | 0.498 5 | 0.197 5 | 1.058 5 | 1.060 5 | 0.188 9 | 1.233 8 | 1.173 5 | −4.887 3 |
| 25 | 0.501 8 | 0.500 5 | 1.097 2 | 1.095 3 | −0.173 2 | 1.049 5 | 1.055 9 | 0.610 5 |
| 30 | 0.503 1 | 0.999 0 | 1.165 2 | 1.157 2 | −0.688 6 | 1.060 9 | 1.087 2 | 2.479 0 |
| 40 | 0.997 4 | 1.068 6 | 1.185 6 | 1.183 4 | −0.185 6 | 0.974 0 | 0.987 0 | −1.334 7 |
| 50 | 0.998 6 | 1.658 3 | 1.247 0 | 1.254 9 | 0.633 5 | 0.928 7 | 0.950 1 | 2.304 3 |
| 60 | 1.012 1 | 2.107 7 | 1.291 9 | 1.308 9 | 1.315 9 | 0.902 0 | 0.886 2 | −1.751 7 |
| 15 | 1.997 6 | 0.205 1 | 1.126 1 | 1.126 7 | 0.053 3 | 1.477 0 | 1.430 0 | −3.182 1 |
| 25 | 2.004 4 | 1.008 7 | 1.230 2 | 1.225 9 | −0.349 5 | 1.437 2 | 1.449 2 | 0.835 0 |
| 30 | 1.999 9 | 1.483 8 | 1.286 1 | 1.284 5 | −0.124 4 | 1.467 6 | 1.482 8 | 1.035 7 |
| 40 | 1.503 9 | 0.199 1 | 1.094 5 | 1.093 9 | −0.054 8 | 0.836 4 | 0.858 5 | 2.642 3 |
| 50 | 1.500 5 | 1.024 0 | 1.198 1 | 1.195 4 | −0.225 4 | 0.857 9 | 0.873 2 | 1.783 4 |
| 60 | 1.507 3 | 1.594 3 | 1.262 0 | 1.264 6 | 0.206 0 | 0.859 7 | 0.837 3 | −2.605 6 |
| 15 | 2.501 5 | 0.501 1 | 1.187 0 | 1.186 6 | −0.033 7 | 1.681 3 | 1.638 2 | −2.563 5 |
| 25 | 2.497 0 | 0.800 0 | 1.222 1 | 1.220 5 | −0.130 9 | 1.448 4 | 1.471 1 | 1.566 2 |
| 30 | 2.501 5 | 1.199 3 | 1.266 0 | 1.269 8 | 0.300 2 | 1.435 5 | 1.480 2 | 3.113 9 |
| 40 | 3.007 8 | 0.199 6 | 1.163 3 | 1.159 4 | −0.335 3 | 1.026 9 | 1.045 1 | 1.772 3 |
| 50 | 3.000 9 | 0.808 7 | 1.230 2 | 1.233 0 | 0.227 6 | 0.996 6 | 1.009 6 | 1.304 4 |
| 60 | 3.007 8 | 0.993 5 | 1.247 0 | 1.252 8 | 0.465 1 | 0.899 4 | 0.883 8 | −1.734 5 |

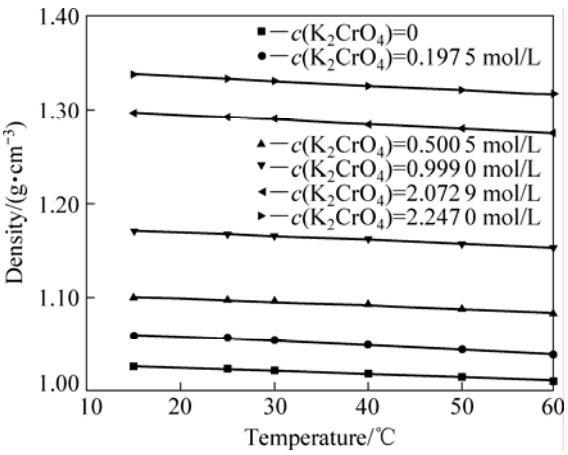


**Fig.1** Effect of temperature on solution density at KOH of 0.5 mol/L

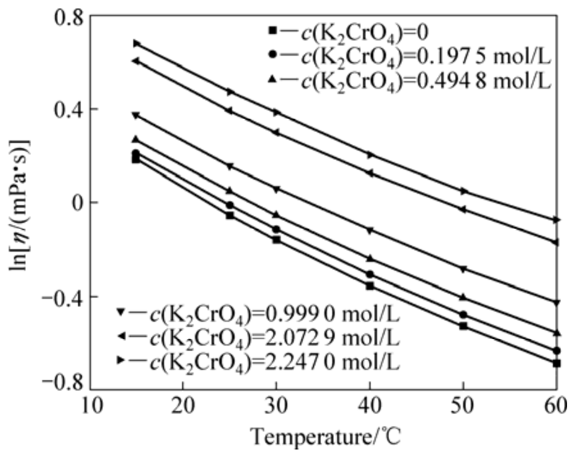


**Fig.3** Effect of temperature on solution viscosity at KOH of 0.5 mol/L

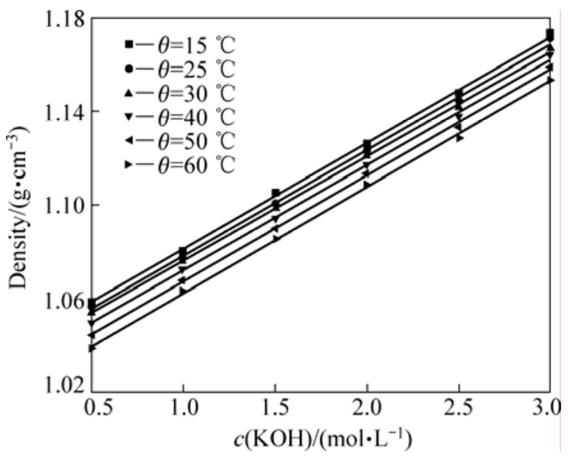


**Fig.2** Effect of hydroxide concentration on solution density under different temperatures at $K_2CrO_4$ of 0.2 mol/L

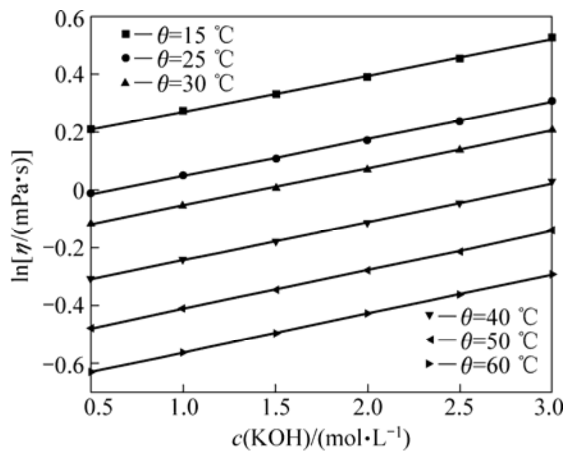


**Fig.4** Effect of hydroxide concentration on solution viscosity under different temperature at $K_2CrO_4$ of 0.2 mol/L

7.669 0% at $\theta$=40 ℃, $c(KOH)$=1.508 4 mol/L and $c(K_2CrO_4)$=1.788 1 mol/L and the others are all below 5.8%. This semi-empirical equation for viscosity can meet the needs for industrial application.

## 4 Conclusions

1) Regression equations for viscosity and density are obtained with the least-squares method and the average errors between the calculated and experimental data are 0.341 0% for densities (with maximum value of 1.315 9%) and 1.144 7% (with maximum value of 7.669 0%) for viscosities, respectively.

2) The semi-empirical equations obtained can be used over the range of experimental conditions (15 ℃$\leq\theta\leq$60 ℃, 0.5 mol/L$\leq c(KOH)\leq$3 mol/L and 0$\leq c(K_2CrO_4)<$ Saturation) and will be helpful and instructive to industrial application.

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