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Densities and Viscosities of Chromium Trioxide + Potassium Chromate + Potassium Dichromate + Water from (298.15 to 333.15) K

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Densities and viscosities of chromium trioxide + potassium chromate + potassium dichromate + water quaternary mixtures and potassium chromate + potassium dichromate + water ternary mixtures have been measured from (298.15 to 333.15) K. The dependence of density and viscosity on temperature and concentration has been correlated. Apparent molar volumes, standard partial molar volumes, and the viscosity *B*-coefficient of chromium trioxide were calculated from the experimental measurements. The solute-mixed solvent interaction, solute–solute interaction, and structure-making effect of chromium trioxide have been discussed using the Helper equation and the Jones−Dole equation. The relationship between relative changes in viscosity and solute-mixed solvent interaction has been probed.

Introduction

Density and viscosity are basic data used in chemical engineering designs, process optimization, and molecular thermodynamics study of solution.[1]&–;[5] Chromium trioxide, potassium chromate, potassium dichromate, etc. are chromium compounds that are important basis chemical products, widely used in chemical engineering, metallurgy, plating, machine, leather, pigment, printing, rubber, antisepsis, grease refining, and the drug industry, and so on. Their advanced commercial production, process plan, environmental technological, and process application urgently need the basic data of density and viscosity and so on for chromium trioxide, potassium chromate, and potassium dichromate in aqueous and mixed aqueous solution.[6]&–;[10] Iadicicco et al.[11] have measured densities and viscosities for aqueous solutions of potassium chromate at $T =$ 25 °C. Hartford et al.[12] have measured densities at $T =$ (15.6 to 50) °C and viscosities at $T =$ (25, 40, and 75) °C for both potassium dichromate aqueous solution and potassium chromate aqueous solution, respectively. Szewczyk et al.[13] and Postnikov[14] have measured densities and viscosities for saturated potassium dichromate aqueous solution at $T =$ (21.15 to 60.2) °C and $T =$ (20 to 80) °C, respectively. Kudryashov et al.[15] have measured densities for the potassium chromate + potassium dichromate + water system at $T =$ (25, 50, and 75) °C. However, density and viscosity data of ternary and quaternary systems are scare over a wide temperature range. This paper is a continuation of our previous work.[6]&–;[10] In this study, densities and viscosities of potassium chromate + potassium dichromate + water (PDW) ternary mixtures and chromium trioxide + potassium chromate + potassium dichromate + water (CPDW) quaternary mixtures have been measured from (298.15 to 333.15) K. From experimental measurements of densities and viscosities, apparent molar volumes, standard partial molar volumes, and the viscosity *B*-coefficient of chromium trioxide were calculated. The solute-mixed solvent interaction, solute–solute interaction, and structure-making effect of chromium trioxide have been discussed.

Experimental Section

Materials. Chromium trioxide obtained from the Tianjing Fuchen Chemical Reagent Co. was of AR grade, and its purity was greater than 99.0 % by mass. Potassium chromate obtained from the Tianjing Yongda Chemical Reagent Co. was of AR grade, and its purity was greater than 99.5 % by mass. Potassium dichromate obtained from the Tianjing Fuchen Chemical Reagent Co. was of AR grade, and its purity was greater than 99.8 % by mass. These materials were dried in a vacuum drier for 3 days before use. The double-distilled water used in the experiments was deionized. The conductivity was less than $1•;10^{-4}$ $\mathrm{S \cdot m^{-1}}$.

Preparing Solution. First of all, the binary mixed solvents of potassium chromate + water were prepared by mixing appropriate masses using an electronic balance (type AW120, Shimadzu Co.), and the molality of potassium chromate was 0.1667 $\mathrm{mol \cdot kg^{-1}}$ for the binary mixed solvent of potassium chromate + water. The balance had an uncertainty of ± 0.1 mg. Then, a series of PDW ternary solutions were prepared by adding potassium dichromate of an appropriate mass into the mixed solvent of a known mass. The molality of potassium dichromate in the PDW solution was referred to as m_k ($\mathrm{mol \cdot kg^{-1}}$). Then, a series of CPDW quaternary solutions were prepared by adding chromium trioxide of an appropriate mass into PDW solutions at a definite m_k. The molality of chromium trioxide in the CPDW solution was referred to as m ($\mathrm{mol \cdot kg^{-1}}$). The prepared CPDW solution was about 300 mL at a time, generally, in order to finish measurements of density and viscosity simultaneously.

Measurements of Densities. Densities were measured using three 25 $\mathrm{cm^3}$ pycnometers with an internal capillary diameter of about 1 mm. The internal volumes of the pycnometer were calibrated with double-distilled water at each of the measured temperatures. The densities of water were taken from Lange's Handbook of Chemistry.[16] The thoroughly cleaned and perfectly dried pycnometers were first weighed on an electronic balance and then filled with experimental solutions and immersed in a thermostat (type 501, Shanghai Laboratory Instrument Works Co., Ltd.) controlled to within ± 0.02 K. After thermal equilibrium had been achieved at the required temperature, the

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Table 1. Comparison of Experimental Density ρ, and Viscosity η of Potassium Dichromate +Water and Potassium Chromate +Water with Literature Data

		ρ/ g·cm^{-3}				η/mPa·s	
solution	T/K	exptl	lit.	solution	T/K	exptl	lit.
2.0 wt % $K_2Cr_2O_7$ + H_2O	313.15	1.0065	1.006[19]	4.78 wt % $K_2Cr_2O_7$ + H_2O	313.15	0.6465	0.65[12]
	333.15	0.9970	0.996[19]	9.06 wt % $K_2Cr_2O_7$ + H_2O	313.15	0.6805	0.68[12]
5.0 wt % $K_2Cr_2O_7$ + H_2O	313.155	1.0268	1.026[19]	9.31 wt % K_2CrO_4 + H_2O	298.15	0.9285	0.93[12]
	333.15	1.0164	1.017[19]		313.15	0.7309	0.73[12]
4.9 wt % K_2CrO_4 + H_2O	298.15	1.0346	1.034968[11]				
5.38 wt % K_2CrO_4 + H_2O	298.15	1.0383	1.038265[11]				
6.53 wt % K_2CrO_4 + H_2O	298.15	1.0468	1.046724[11]				
15.5 wt % $K_2Cr_2O_7$ + H_2O	319.15	1.1665	1.1663[13]	15.5 wt % $K_2Cr_2O_7$ + H_2O	319.15	0.6914	0.6939[13]
17.2 wt % $K_2Cr_2O_7$ + H_2O	323.25	1.1842	1.1847[13]	17.2 wt % $K_2Cr_2O_7$ + H_2O	323.25	0.6658	0.6682[13]
21.4 wt % $K_2Cr_2O_7$ + H_2O	333.35	1.2321	1.2318[13]	21.4 wt % $K_2Cr_2O_7$ + H_2O	333.35	0.6307	0.6294[13]

pycnometers were removed from the thermostat and properly cleaned, dried, and weighed. The density was then determined from the mass of the sample and the volume of the pycnometers. The readings from three pycnometers were averaged to determine the density. The uncertainty analysis was based upon the International Guide to the Expression of the Uncertainty in Measurement.[17] Uncertainties in the density measurement were within ± 0.0002 g·cm^{-3} on the basis of the 95 % confidence level. The errors were caused mainly by the weighing process, repeatability of the measurement, and glassware.

Measurements of Viscosities. Viscosity was measured using a commercial Ubbelohde capillary viscometer (type 1836-A, Shanghai Glass Instruments Factory, China) of 0.55 mm diameter, calibrated with double-distilled water at (298.15, 303.15, 313.15, 323.15, and 333.15) K. A thoroughly cleaned and perfectly dried viscometer, filled with experimental solutions, was placed exactly vertical in an insulated jacket, wherein constant temperature (± 0.02 K) was maintained by circulating water from a thermoelectric controller (type 501, Shanghai Laboratory Instrument Works Co., Ltd.) at the required temperature. After thermal stability was attained, the flow times of the solutions were recorded with an electronic digital stopwatch correct to ± 0.01 s. At least five repetitions of each datum point obtained were reproducible to ± 0.06 s, and the results were averaged. Because all flow times were greater than 200 s and the capillary diameter (0.55 mm) was far less than its length [(90 to 100) mm], the kinetic energy and end corrections, respectively, were found to be negligible. The viscosity was then calculated from the relationship[18]

$$\eta/\eta_w = (\rho t)/(\rho_w t_w) \tag{1}$$

where ρ, η, t, and ρ_w, η_w, t_w refer to the density, viscosity, and flow time of solution and water, respectively. The values of viscosity and density of pure water come from Lange's Handbook of Chemistry.[16] The uncertainty in the viscosity measurement was estimated on the basis of the principle of error propagation to be ± 0.6 % at the 95 % confidence level. There are three main sources of error in the measurement of the viscosity. The first is the propagation error resulting from the measurement of the density. The second is the measurement error resulting from the weighing process of the sample and the repeatability of the measurement. The third is instrument error.

Experiment Reliability Proof. The measured densities and viscosities of potassium dichromate + water and potassium chromate + water at various concentrations and at different temperatures have been compared with literature values. Some results are included in Table 1. It can be seen that our experimental values of densities and viscosities are in good agreement with those reported in the literature.[11&–;13,19]

Results and Discussion

The experimental densities and viscosities at various temperatures as a function of molality for chromium trioxide in PDW ternary mixtures are presented in Table 2. It can be seen that density and viscosity decrease with increasing temperature at a definite m_k in PDW ternary mixtures and increase with an increase in m_k at a definite temperature in PDW ternary mixtures. The density and viscosity decrease with increasing temperature at a definite m in CPDW quaternary mixtures and increase with an increase in m at a definite temperature in CPDW quaternary mixtures.

Correlation of Density. The dependence of density on temperature and concentration has been correlated by means of the two-variable fitting method,[20] and the following equation is obtained from the experimental data.

$$\rho = (1.022 + 0.1951 m_k) + DA^b + \frac{T^a - 298.15^a}{333.15^a - 298.15^a}(FA^c - DA^b - 0.014 - 0.0042 m_k) \tag{2}$$

$$D = 0.043 - 0.0181 m_k$$

$$F = 0.041 - 0.0138 m_k$$

$$A = m/(0.6451 - 0.1781 m_k)$$

where ρ is the density of the mixtures; m_k is the molality of potassium dichromate; m is the molality of chromium trioxide; T is the absolute temperature; and a, b, and c are curve-fit parameters. The values are listed in Table 3, along with their standard deviation and average relative deviation. Densities of PDW ternary mixtures and CPDW quaternary mixtures are calculated according to eq 2 using values for parameters a, b, and c that are listed in Table 3. Some results can be seen in Figure 1. From comparison of the calculated and experimental values, the total standard deviation (SD) and average relative deviations (ARD) of 240 data points are 0.0005 g·cm^{-3} and 0.037 %, respectively. It is clear that eq 2 can be successfully used to correlate densities of PDW ternary mixtures and CPDW quaternary mixtures.

The standard deviation (SD) and average relative deviations (ARD) are defined as

$$\mathrm{SD} = \left(\sum (Y^{\mathrm{exptl}} - Y^{\mathrm{calcd}})^2/(p - n)\right)^{1/2} \tag{3}$$

$$\mathrm{ARD} = \frac{1}{p}\sum \frac{|Y^{\mathrm{calcd}} - Y^{\mathrm{exptl}}|}{Y^{\mathrm{exptl}}} \tag{4}$$

where p represents the number of experimental points and n is the number of parameters. Y^{calcd} and Y^{exptl} refer to the calculated values from the equation and the experimental values, respectively.

Table 2. Experimental Densities ρ, Viscosities η, and Apparent Molar Volume V_φ of PDW Ternary Mixtures and CPDW Quaternary Mixtures as a Function of Molality from T = (298.15 to 333.15) K

m	ρ/g·cm^{-3} at T/K					η/mPa·s at T/K					V_φ/cm^3·mol^{-1} at T/K				
mol·kg^{-1}	298.15	303.15	313.15	323.15	333.15	298.15	303.15	313.15	323.15	333.15	298.15	303.15	313.15	323.15	333.15
m_k = 0.0258 mol·kg^{-1}															
0.0000	1.0269	1.0256	1.0220	1.0178	1.0131	0.8925	0.8111	0.6691	0.5657	0.4879					
0.1282	1.0335	1.0320	1.0283	1.0239	1.0191	0.8969	0.8148	0.6719	0.5680	0.4897	48.23	49.71	50.46	51.98	52.77
0.2563	1.0417	1.0402	1.0363	1.0318	1.0270	0.9039	0.8198	0.6758	0.5713	0.4933	42.01	42.73	43.81	44.90	45.24
0.3845	1.0508	1.0490	1.0452	1.0407	1.0359	0.9105	0.8272	0.6813	0.5758	0.4961	37.55	38.75	39.18	39.85	40.02
0.5126	1.0601	1.0582	1.0544	1.0498	1.0447	0.9192	0.8343	0.6883	0.5818	0.5003	34.83	35.82	36.18	36.83	37.47
0.6408	1.0696	1.0677	1.0637	1.0591	1.0540	0.9273	0.8412	0.6928	0.5852	0.5050	32.82	33.65	34.14	34.62	35.09
m_k = 0.0516 mol·kg^{-1}															
0.0000	1.0320	1.0306	1.0273	1.0229	1.0179	0.8962	0.8125	0.6703	0.5665	0.4892					
0.1272	1.0386	1.0370	1.0336	1.0291	1.0240	0.9007	0.8163	0.6732	0.5688	0.4910	47.70	49.34	50.09	50.86	51.64
0.2544	1.0469	1.0453	1.0418	1.0372	1.0319	0.9075	0.8213	0.6772	0.5727	0.4941	41.01	41.98	42.72	43.42	44.51
0.3816	1.0559	1.0542	1.0506	1.0459	1.0407	0.9168	0.8293	0.6824	0.5772	0.4974	37.12	37.92	38.60$^-$	39.26	39.70
0.5088	1.0650	1.0632	1.0594	1.0547	1.0495	0.9235	0.8365	0.6896	0.5828	0.5015	34.80	35.57	36.41	36.87	37.14
0.6360	1.0740	1.0723	1.0682	1.0634	1.0578	0.9319	0.8429	0.6942	0.5864	0.5057	33.46	33.92	35.00	35.48	36.26
m_k = 0.0773 mol·kg^{-1}															
0.0000	1.0372	1.0358	1.0319	1.0275	1.0230	0.8994	0.8127	0.6703	0.5685	0.4903					
0.1262	1.0437	1.0421	1.0380	1.0335	1.0289	0.9039	0.8167	0.6735	0.5708	0.4922	48.24	49.72	51.22	52.00	52.78
0.2525	1.0519	1.0502	1.0460	1.0415	1.0367	0.9113	0.8218	0.6767	0.5736	0.4942	41.70	42.78	43.88	44.19	45.29
0.3787	1.0608	1.0589	1.0548	1.0502	1.0454	0.9197	0.8300	0.6826	0.5784	0.4987	37.63	38.82	39.25	39.67	40.35
0.5050	1.0698	1.0680	1.0638	1.0590	1.0540	0.9273	0.8361	0.6899	0.5835	0.5029	35.29	35.98	36.45	37.09	37.94
0.6312	1.0788	1.0770	1.0726	1.0675	1.0624	0.9371	0.8446	0.6948	0.5887	0.5068	33.79	34.33	34.97	35.90	36.69
m_k = 0.1031 mol·kg^{-1}															
0.0000	1.0430	1.0414	1.0374	1.0330	1.0281	0.9002	0.8135	0.6732	0.5701	0.4922					
0.1253	1.0492	1.0475	1.0433	1.0388	1.0338	0.9047	0.8175	0.6764	0.5725	0.4940	50.14	50.83	52.34	53.12	53.93
0.2506	1.0573	1.0555	1.0512	1.0467	1.0416	0.9109	0.8231	0.6811	0.5766	0.4971	42.86	43.55	44.63	44.97	45.70
0.3760	1.0659	1.0642	1.0600	1.0553	1.0502	0.9192	0.8322	0.6864	0.5821	0.5012	39.04	39.24	39.66	40.34	40.89
0.5013	1.0750	1.0732	1.0689	1.0642	1.0591	0.9281	0.8388	0.6931	0.5863	0.5055	36.09	36.41	36.87	37.34	37.61
0.6266	1.0839	1.0821	1.0778	1.0730	1.0678	0.9383	0.8473	0.7005	0.5928	0.5106	34.49	34.76	35.11	35.59	35.93
m_k = 0.1289 mol·kg^{-1}															
0.0000	1.0479	1.0463	1.0421	1.0374	1.0325	0.9032	0.8163	0.6756	0.5715	0.4924					
0.1244	1.0541	1.0524	1.0480	1.0432	1.0382	0.9077	0.8200	0.6785	0.5738	0.4942	49.74	50.48	51.98	52.77	53.57
0.2488	1.0622	1.0604	1.0560	1.0511	1.0460	0.9153	0.8267	0.6838	0.5785	0.4980	42.50	43.21	43.96	44.63	45.35
0.3732	1.0710	1.0691	1.0647	1.0597	1.0546	0.9242	0.8351	0.6904	0.5837	0.5022	38.21	38.91	39.33	40.00	40.43
0.4976	1.0800	1.0780	1.0737	1.0687	1.0635	0.9334	0.8439	0.6956	0.5886	0.5066	35.58	36.27	36.43	36.83	37.28
0.6220	1.0885	1.0865	1.0821	1.0772	1.0721	0.9436	0.8508	0.7040	0.5948	0.5117	34.63	35.18	35.37	35.56	35.75
m_k = 0.1547 mol·kg^{-1}															
0.0000	1.0530	1.0512	1.0470	1.0422	1.0374	0.9069	0.8229	0.6778	0.5755	0.4976					
0.1235	1.0591	1.0572	1.0529	1.0479	1.0430	0.9115	0.8268	0.6810	0.5780	0.4996	50.12	51.03	51.63	52.79	53.96
0.2470	1.0672	1.0652	1.0609	1.0559	1.0509	0.9195	0.8327	0.6856	0.5821	0.5027	42.53	43.33	43.58	44.11	45.01
0.3705	1.0761	1.0741	1.0696	1.0643	1.0593	0.9278	0.8404	0.6912	0.5869	0.5065	37.89	38.40	39.01	39.97	40.60
0.4940	1.0849	1.0828	1.0784	1.0732	1.0680	0.9376	0.8489	0.6985	0.5932	0.5122	35.64	36.18	36.37	37.03	37.71
0.6175	1.0933	1.0912	1.0866	1.0815	1.0764	0.9483	0.8576	0.7058	0.5990	0.5168	34.76	35.19	35.59	35.95	36.28
m_k = 0.1805 mol·kg^{-1}															
0.0000	1.0571	1.0559	1.0519	1.0475	1.0423	0.9173	0.8261	0.6796	0.5769	0.4994					
0.1226	1.0632	1.0619	1.0578	1.0533	1.0481	0.9229	0.8308	0.6832	0.5798	0.5018	49.78	50.34	51.28	51.94	52.41
0.2452	1.0715	1.0700	1.0659	1.0614	1.0561	0.9306	0.8370	0.6879	0.5836	0.5049	41.47	42.46	42.88	43.16	43.71
0.3678	1.0802	1.0788	1.0745	1.0700	1.0646	0.9397	0.8448	0.6949	0.5898	0.5103	37.56	37.97	38.69	38.83	39.39
0.4904	1.0891	1.0876	1.0832	1.0786	1.0732	0.9511	0.8537	0.7019	0.5957	0.5152	35.13	35.62	36.35	36.54	36.92
0.6130	1.0977	1.0961	1.0916	1.0868	1.0812	0.9603	0.8634	0.7094	0.6013	0.5200	34.01	34.57	35.20	35.67	36.23
m_k = 0.2066 mol·kg^{-1}															
0.0000	1.0620	1.0606	1.0571	1.0524	1.0480	0.9214	0.8282	0.6800	0.5790	0.5008					
0.1217	1.0681	1.0665	1.0629	1.0581	1.0536	0.9287	0.8335	0.6838	0.5821	0.5034	49.43	50.90	51.79	52.45	53.24
0.2434	1.0762	1.0746	1.0709	1.0660	1.0614	0.9360	0.8399	0.6891	0.5861	0.5069	41.87	42.59	43.36	44.00	44.72
0.3652	1.0846	1.0829	1.0792	1.0742	1.0695	0.9445	0.8476	0.6958	0.5926	0.5117	38.46	39.16	39.64	40.27	40.96
0.4869	1.0928	1.0912	1.0874	1.0825	1.0775	0.9548	0.8558	0.7030	0.5976	0.5162	36.99	37.33	37.82	38.08	39.14
0.6086	1.1007	1.0991	1.0954	1.0904	1.0855	0.9689	0.8679	0.7109	0.6047	0.5225	36.44	36.71	36.96	37.29	37.95

Correlation of Viscosity. The dependence of viscosity on temperature and concentration can be represented by the Vogel&–;Tamman&–;Fulcher (VTF) equation[21]

$$\eta = A\exp\left(\frac{B + Cm}{T - D}\right) \qquad (5)$$

where η is the viscosity of the mixtures; m is molality of chromium trioxide; T is the absolute temperature; and A, B, C, and D are equation parameters. The values are listed in Table 4, along with their SD and ARD. Some results can be seen in Figure 2. From comparison of the calculated and experimental values, the total SD and ARD of 240 data points are 0.0017 mPa·s and 0.20 %, respectively. On the basis of the obtained SD and ARD values, we conclude that eq 5 can be successfully used for the correlation of viscosity.

Apparent Molar Volume. The apparent molar volume, V_φ, of chromium trioxide in the CPDW quaternary mixtures is given by the following equation[21]

Table 3. Parameters of Equation 2, Average Relative Deviation, ARD, and Standard Deviation, SD, for Eight Different Molalities, m_k, of Potassium Dichromate for PDW Mixed Solvent

m_k				10^2ARD	10^4SD
mol·kg^{-1}	a	b	c	%	g·cm^{-3}
0.0258	5.000	1.151	1.176	1.8	2.6
0.0516	7.000	1.122	1.125	2.0	2.8
0.0773	4.850	1.137	1.140	2.2	2.9
0.1031	4.500	1.142	1.167	6.3	7.5
0.1289	4.600	1.146	1.165	5.3	7.1
0.1547	3.500	1.122	1.152	4.3	6.0
0.1805	6.500	1.119	1.119	4.1	5.6
0.2066	5.800	1.087	1.108	4.0	5.6

Table 4. Parameters of Equation 5, Average Relative Deviation, ARD, and Standard Deviation, SD, for Eight Different Molalities m_k, of Potassium Dichromate for PDW Mixed Solvent

m_k	10^2A	B	C	D	10ARD	10^3SD
mol·kg^{-1}	mPa·s	K	K·kg·mol^{-1}	K	%	mPa·s
0.0258	2.480	615.6	10.56	126.4	2.3	2.1
0.0516	3.100	533.4	10.02	139.6	1.8	1.8
0.0773	4.130	438.4	9.320	155.8	1.7	1.5
0.1031	3.410	505.9	10.70	143.5	1.8	1.5
0.1289	3.140	532.9	11.59	139.4	1.6	1.4
0.1547	4.001	456.4	10.76	151.8	2.5	2.3
0.1805	6.150	326.2	9.500	177.3	1.8	1.7
0.2066	7.240	283.3	9.190	186.7	2.2	2.0

$$V_\varphi = \frac{M}{\rho} - \frac{10^3(\rho - \rho_0)}{m\rho\rho_0} \tag{6}$$

where M and m are the molar mass and molality of chromium trioxide, respectively. ρ and ρ_0 are the densities of the solution and mixed solvent, respectively. Values of the apparent molar volume for chromium trioxide have also been given in Table 2. The apparent molar volume increases as temperature increases at a fixed concentration of chromium trioxide and decreases with concentration at a fixed temperature. These values are important because they form the basis for understanding molecular interactions.

The dependence of the apparent molar volume on concentration of the solute reflects solute&–;solute interactions. The apparent molar volume of the solute at infinite dilution that is equal in value to the standard partial molar volume of solute embodies the solute&–;solvent interaction.

The dependence of V_φ for chromium trioxide in a PDW mixed solvent on molality at a definite temperature was fitted with the following expression[21]

$$V_\varphi = V_\varphi{}^0 + A_V \cdot m^{1/2} + B_V \cdot m \tag{7}$$

where $V_\varphi{}^0$ is the standard partial molar volume of solute and A_V is the Debye&–;Huckel limiting law slope for apparent molar volume. It measures the solute&–;solute interaction. B_V is an empirical constant which depends on solute, solvent, and temperature.

According to eq 7, the fitted $V_\varphi{}^0$, A_V, and B_V of chromium trioxide at various temperatures and concentrations in different PDW mixed solvents obtained by the least-squares method from the experimental data are listed in Table 5.

From the results of Table 5, it is shown that all standard partial molar volumes, $V_\varphi{}^0$, are positive, indicating solvent molecules loosely attached to the solute which expands with increasing temperature, thus resulting in higher values of $V_\varphi{}^0$ at a higher temperature. At a particular temperature, $V_\varphi{}^0$ increases with an increase in m_k. It is suggested that the solute−mixed solvent interaction increases with increasing m_k.

The negative value of A_V for all systems reveals weaker solute interactions. A_V decreasing with increasing m_k indicates solute&–;solute interactions decreasing with increasing m_k. A_V decreasing with an increase in temperature is attributed to more violent thermal agitation at a higher temperature, resulting in diminishing force of the solute&–;solute interactions.

The variation of $V_\varphi{}^0$ with temperature can be expressed by a second-degree polynomial as

$$V_\varphi{}^0 = \sum_{i=0}^{2} a_i T^i \tag{8}$$

over the temperature range under investigation. The coefficients, a_i, are presented in Table 6. At a constant pressure, the standard partial molar volume expansibility may be obtained from the differential to eq 8

$$\left(\frac{\partial V_\varphi^0}{\partial T}\right)_p = a_1 + 2a_2 T \tag{9}$$

It is observed that all standard partial molar volume expansibilities are positive over the temperature range under investigation, and $(\partial V_\varphi{}^0/\partial T)_P$ increases with an increase of temperature. These results can be ascribed to the presence of a caging effect.[22]

For determining structure-making and structure-breaking capacities of the solute in different mixed solvents, the following equation of Hepler[23] was used

$$(\partial C_p/\partial p)_T = -(\partial^2 V_\varphi{}^0/\partial T^2)_P \tag{10}$$

The values in eq 10 are also listed in Table 6. It can be seen that all $(\partial^2 V_\varphi{}^0/\partial T^2)_P$are positive over the temperature range

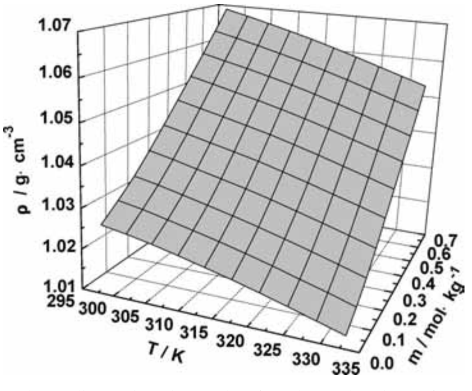

Figure 1. Three-dimensional graphs for dependencies of densities on temperature and molality of chromium trioxide for CPDW quaternary mixtures at m_k = 0.0258 mol·kg^{-1}.

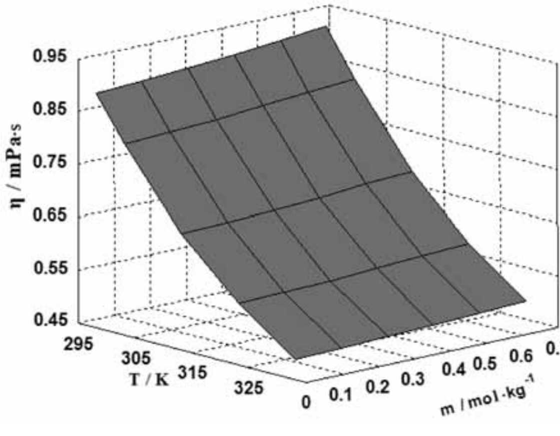

Figure 2. Three-dimensional graphs for dependencies of viscosities on temperature and molality of chromium trioxide for CPDW quaternary mixtures at m_k = 0.0258 mol·kg^{-1}.

Table 5. Standard Partial Molar Volume V_φ^0, Debye&–;Huckel Limiting Law Slope A_V, and Empirical Constant B_V of Chromium Trioxide in PDW Ternary Mixed Solvent at Different Temperatures

m_k	$V_\varphi^0/\mathrm{cm^3 \cdot mol^{-1}}$ at T/K					$A_V/\mathrm{cm^3 \cdot kg^{1/2} \cdot mol^{-3/2}}$ at T/K					$B_V/\mathrm{cm^3 \cdot kg \cdot mol^{-2}}$ at T/K				
$\mathrm{mol \cdot kg^{-1}}$	298.15	303.15	313.15	323.15	333.15	298.15	303.15	313.15	323.15	333.15	298.15	303.15	313.15	323.15	333.15
0.0258	70.00	71.19	72.84	74.72	77.25	−71.78	−72.44	−74.21	−75.13	−81.83	31.75	32.41	32.42	31.15	36.33
0.0516	72.10	73.48	75.33	77.04	80.13	−83.49	−83.98	−88.68	−90.92	−99.16	43.73	43.10	47.96	48.73	55.04
0.0773	73.08	74.45	76.43	79.05	82.14	−84.12	−84.65	−87.03	−94.74	−102.6	43.52	43.04	43.86	50.54	56.99
0.1031	74.92	76.26	78.38	80.94	84.09	−85.49	−87.54	−90.80	−96.34	−104.3	43.47	44.29	43.70	49.21	54.89
0.1289	77.50	78.59	80.23	82.34	85.12	−97.94	−99.61	−99.51	−104.4	−110.2	55.06	56.52	53.64	57.12	60.31
0.1547	80.21	81.05	82.33	84.35	86.68	−107.4	−107.2	−110.0	−113.1	−116.9	62.84	61.90	63.92	65.42	67.14
0.1805	80.86	81.81	83.32	85.35	87.91	−112.5	−113.2	−116.0	−121.9	−129.5	67.38	67.52	69.74	74.57	81.07
0.2066	81.83	82.99	84.55	86.69	89.57	−120.4	−119.6	−121.1	−126.0	−133.8	80.11	77.22	77.28	80.58	87.37

Table 6. Regression Coefficients and Standard Deviation, SD, of Equation 8 and Term $(\partial^2 V_\varphi^0/\partial T)_P$ for Eight Different Molalities, m_k, of Potassium Dichromate for PDW Mixed Solvent

m_k				SD	$10^3(\partial^2 V_\varphi^0/\partial T)_P$
$\mathrm{mol \cdot kg^{-1}}$	a_0	a_1	$10^3\ a_2$	$\mathrm{cm^3 \cdot mol^{-1}}$	$\mathrm{cm^6 \cdot mol^{-2} \cdot K^{-2}}$
0.0258	126.0	−0.5349	1.165	0.22	2.330
0.0516	156.5	−0.7303	1.503	0.41	3.006
0.0773	171.7	−0.8530	1.753	0.17	3.506
0.1031	188.2	−0.9487	1.910	0.15	3.820
0.1289	208.3	−1.0210	1.954	0.15	3.908
0.1547	229.1	−1.1090	2.045	0.14	4.090
0.1805	230.4	−1.1270	2.098	0.12	4.196
0.2066	232.9	−1.1510	2.163	0.23	4.326

under investigation, indicating obvious structure-making tendency of the chromium trioxide in the CPDW quaternary mixtures.

Relative Changes in Viscosity and the Viscosity B-Coefficient. The relative changes in viscosity of chromium trioxide dissolution in PDW ternary mixed solvents were calculated from the following equation

$$\Delta\eta = \frac{\eta - \eta_0}{\eta_0} = \frac{\eta}{\eta_0} - 1 \tag{11}$$

where η and η_0 are viscosities of CPDW solutions and PDW mixed solvents, respectively. $\Delta\eta$ is calculated from the experimental data by eq 11. Some results of $\Delta\eta$ are shown in Figure 3. It can be seen that $\Delta\eta$ increases with increasing molality of chromium trioxide and decreases with increasing temperature, which indicates that solute−mixed solvent interaction is enhanced with increasing molality of chromium trioxide and weakened with increasing temperature.

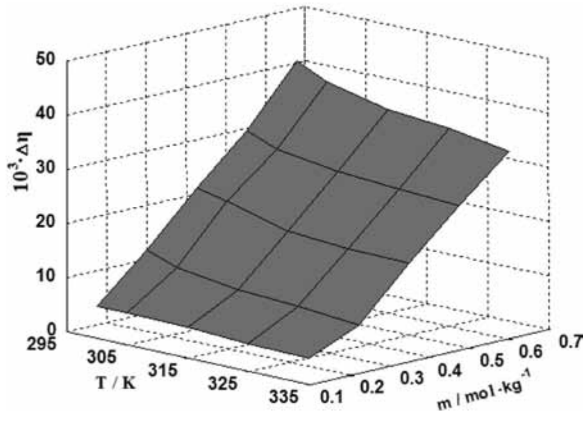

Figure 3. Three-dimensional graphs for dependencies of relative changes in viscosity on temperature and molality of chromium trioxide for CPDW quaternary mixtures at $m_k = 0.0773\ \mathrm{mol \cdot kg^{-1}}$.

The η/η_0 in eq 11 is relative viscosity, η_r. The relationship between η_r and molarity of the solute can be represented using the following Jones-Dole equation[24]

Table 7. Viscosity *B*-Coefficients of Chromium Trioxide in PDW Ternary Mixed Solvent

m_k	$B/\mathrm{cm^3 \cdot mol^{-1}}$ at T/K				
$\mathrm{mol \cdot kg^{-1}}$	298.15	303.15	313.15	323.15	333.15
0.0258	97.56	96.97	95.98	93.08	90.33
0.0516	99.48	98.56	96.63	94.59	91.54
0.0773	107.6	102.7	101.6	99.68	95.57
0.1031	116.0	111.6	110.0	107.4	105.7
0.1289	122.4	117.7	115.1	111.7	109.8
0.1547	126.1	119.3	117.5	116.4	113.5
0.1805	128.0	124.7	123.3	119.8	117.4
0.2066	133.2	129.3	126.1	123.6	120.1

$$\eta_r = \frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc \tag{12}$$

where c is molarity (calculated from molality) of chromium trioxide in the solution. B refers to the viscosity B-coefficient of solute. It reflects the size and shape effect of a solute, structure effect, and solvation effect caused by solute&–;solvent interaction. It is a main contributer to η_r.

Viscosity B-coefficients obtained by a computerized least-squares procedure from the experimental data are listed in Table 7. It can be seen that the viscosity B-coefficients decrease with increasing temperature, namely exhibiting a negative dB/dT. The dB/dT values are known to be a better criterion for determining the structure effect of the solute on solvent. Structure-making solutes should have a negative value and structure- breaking solutes a positive value. The negative dB/dT values of chromium trioxide in PDW mixed solvents indicate that chromium trioxide acts as a structure-maker to mixed solvents. The solute−mixed solvent interaction intensifies the structure of solution. It conforms to the results obtained by volume properties.

Literature Cited

(1) Prausniutz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed.; Prentice-Hall PTR: Upper Saddle River, NJ, 1999.
(2) Wang, F. A.; Jiang, Y. L. *Molecular Thermodynamics and Chromatographic Retention*; Meteorology Press: Beijing, 2001.
(3) Huque, M.; Siddiquey, I. A.; Uddin, M. N. Physico-Chemical Study of Aqueous Solutions of Electrolytes in Mixed Solvents. *J. Chem. Thermodyn.* **2006**, *38*, 1474–1478.
(4) Hervello, M. F.; Sa′nchez, A. Densities of Univalent Cation Sulfates in Ethanol + Water Solutions. *J. Chem. Eng. Data* **2007**, *52*, 752–756.
(5) Abdulagatov, I. M.; Azizov, N. D. Experimental Study of the Effect of Temperature, Pressure, and Concentration on the Viscosity of Aqueous $SrCl_2$ Solutions in the Range of (293 to 473) K and (0.1 to 20) MPa. *J. Chem. Eng. Data* **2007**, *52*, 841–850.
(6) Zhang, Y.; Li, Z. H.; Qi, T.; Zheng, S. L.; Li, H. Q.; Xu, H. P. Green Manufacturing Process of Chromium Compounds. *Environ. Prog.* **2005**, *24*, 44–50.
(7) Li, C. W.; Qi, T.; Wang, F. A.; Zhang, Y.; Yu, Z. H. Variation of Cell Voltage with Rreaction Time in Electrochemical Synthesis Process of Sodium Dichromate. *Chem. Eng. Technol.* **2006**, *29*, 481–486.
(8) Li, C. W.; Yu, Z. H.; Qi, T.; Wang, F. A.; Zhang, Y. Chang of Operating Voltages in Electrochemical Synthesis Process of Chromic Anhydride. *J. Chem. Ind. Eng. (China)* **2006**, *57*, 71–73.

(9) Li, C. W.; Qi, T.; Wang, F. A.; Zhang, Y.; Chen, G. S.; Zhang, P. Macrokinetic Study of the Electrochemical Synthesis Process of Sodium Dichromate. *Chem. Eng. Technol.* **2007**, *30*, 467–473.

(10) Li, C. W.; Qi, T.; Wang, F. A.; Zhang, Y.; Chen, G. S.; Zhang, P. *Study on Green Electrosynthesis of Chromic Anhydride from Potassium Dichromate and Removal of Contaminants in Membrane*,The 233 rd ACS National Meeting, Chicago, IL, March 25&–;29, 2007; American Chemical Society: Washington, DC; PHYS No. 339.

(11) Iadicicco, N.; Paduano, L.; Vitagliano, V. Diffusion Coefficients for the System Potassium Chromate-Water at 25 °C. *J. Chem. Eng. Data* **1996**, *41*, 529–533.

(12) Hartford, W. H. Properties of Technically Important Hexavalent Chromium Compounds. *J. Chem. Ind. Eng.* **1949**, *41*, 1993–1997.

(13) Szewczyk, J.; Sokodowskl, W.; Sangwal, K. Some Physical Properties of Saturated, Supersaturated, and Undersaturated Aqueous Potassium Bichromate Solutions. *J. Chem. Eng. Data* **1985**, *30*, 243–246.

(14) Postnikov, V. A. Density and Viscosity of Saturated Aqueous Solutions of Some Substances. *Zh. Fiz. Khim.* **1970**, *44*, 236–238.

(15) Kudryashov, S. F.; Chirkova, T. Y.; Frolova, S. I. Potassium Chromate (VI)-Potassium Dichromate (VI)-Water System. *Zh. Neorg. Khim.* **1974**, *19*, 1660–1662.

(16) Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed.; McGraw-Hill: New York, 1999.

(17) BIPM; IEC; IFCC; ISO; IUPAC; IUPAP; OIML. *Guide to the Expression of Uncertainty in Measurement*; International Organization for Standardization: Geneva, 1995.

(18) Wang, L. C.; Xu, H. S.; Zhao, J. H.; Song, C. Y.; Wang, F. A. Densities and Viscosities of Niacin + 3-Picoline + Sulfuric Acid + Water from (293.15 to 343.15) K. *J. Chem. Eng. Data* **2005**, *50*, 643–646.

(19) Kearley, R. A. Some Physical Properties of Sodium Chromate, Sodium Dichromate, and Potassium Dichromate, and Their Aqueous Solutions. *J. Chem. Eng. Data* **1964**, *9*, 548–551.

(20) Sohnel, O.; Novotny, P. *Densities of Aqueous Solutions of Inorganic Substances*; Akademia: Prague, 1985.

(21) Horvath, A. L. *Handbook of Aqueous Electrolyte Solutions: Physical Properties, Estimation and Correlation Methods*; Ellis Horwood: Chichester, 1985.

(22) Nikam, P. S.; Sawant, A. B.; Khaltnar, R. S.; Ahere, J. S. Limiting Partial Molar Volumes of $(NH_4)_2SO_4$, K_2SO_4 and $Al_2(SO_4)_3$ in DimethyIsulphoxide + Water at Different Temperatures. *J. Mol. Liq.* **1999**, *81*, 253–260.

(23) Hepler, L. G. Thermal Expansion and Structure in Water and Aqueous Solutions. *Can. J. Chem.* **1969**, *47*, 4613–4617.

(24) Stokes, R. H.; Mills, R. *Viscosity of Electrolytes and Related Properties*; Pergamon Press: New York, 1971.

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