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Electrical Conductivity, Viscosity, and Molar Volume of Potassium Nitrate + Lithium Nitrate + Cadmium Nitrate Tetrahydrate Melt Systems

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Densities, viscosities, and electrical conductivity of potassium nitrate + lithium nitrate + cadmium nitrate tetrahydrate melt systems were measured as functions of temperature ($\approx 292.15 \le T/\mathrm{K} \le 363.15$) and at various compositions *x*. The temperature dependence of viscosity and conductivity has been described by the Vogel−Tammann−Fulcher (VTF) equation. Molar volume data were fitted to an equation similar to the VTF equation based on the free volume model. Viscosity isotherms, unlike electrical conductivity, exhibit both negative as well as positive deviation from linearity as a function of composition. Mixed alkali effect in electrical conductivity has been observed under the isoviscosity condition. The onset of the mixed alkali effect has been explained in terms of the anion polarization model and complex ion of cadmium.

Introduction

Mixed alkali effect (MAE), which is described as the deviation from the additivity in isotherms of transport properties, has been found to a lesser extent (ca. 4%) in hydrate melt and liquid media (Sangma et al., 1984; Islam and Ismail, 1990; Mahiuddin, 1994). On the other hand, the percent deviation from the additivity in transport properties (e.g., viscosity and electrical conductivity) in oxide melt media has been found to be many-fold (Day, 1976; Moynihan and Lesikar, 1981; Jain et al., 1983; Ingram, 1987) in comparison to that in hydrate melt media for the same pair of alkali metal ions. The theory that explains the MAE in oxide melt media where rigid network structure prevails may not be applicable to the mixed alkali systems in hydrate melt media.

Dietzel (1983) has suggested that if the difference between the field strength of cations, $\Delta F = \Delta(Z/a^2)$, where *Z* is the valency of the cation and *a* is the cation−anion distance in 10^{-10} m, is large enough, the MAE concerning transport properties is larger. Maximum efforts have been made to study the MAE by using sodium and potassium cation pairs either in oxide or in hydrate melt media since it has direct relevance to glass technology. In the present article, we have chosen the lithium nitrate + potassium nitrate in cadmium nitrate tetrahydrate melt medium to study the MAE by measuring the electrical conductivity and viscosity as functions of temperature and composition. The difference between the cation field strength, ΔF, in case of the lithium and potassium cation pair is of the order of 0.10−0.14 (Dietzel, 1983), which is higher (2.5 times) than that of the sodium and potassium cation pair.

Experimental Section

Chemicals. Both KNO_3 (E. Merck, 99%) and $LiNO_3$ (Loba, 98%) were recrystallized twice from conductivity water and dried over P_2O_5 in a vacuum desiccator. Cadmium nitrate tetrahydrate (Loba, 99%) was used as such in the molten state. The actual number of moles of water per mole of cadmium nitrate was determined gravimetrically (Vogel, 1969) and was found to be 4.37 ± 0.07.

Apparatus and Procedure. $LiNO_3$ and KNO_3 were found to be soluble up to ≈40 mol % in cadmium nitrate tetrahydrate melt at around 333.15 K. Accordingly, samples were prepared keeping the total alkali ion concentration at 0.3 mole fraction for the $0.3[x\mathrm{KNO_3} + (1 - x)\mathrm{LiNO_3}] + 0.7\mathrm{Cd(NO_3)_2}\cdot 4.37\mathrm{H_2O}$ systems where *x* is the mole fraction of KNO_3 relative to the total mole fraction of potassium/lithium nitrates.

Electrical conductivities (κ) of all solutions were measured (±0.1% accuracy) using a Precision Component Analyzer-6425 (Wayne Kerr) operating in the (2.5×10^{-9}−10) S range with a sensitivity of ±0.01 nS and a platinized platinum electrode (cell constant = 113.5 $\mathrm{m^{-1}}$) with a field frequency of 1.5 kHz. The sample was put in a glass tube with a ground joint, and the conductivity cell was well fitted to prevent evaporation of water. The sample tube was purged with dry nitrogen gas, and the test sample was introduced under nitrogen atmosphere. The conductivity cell was calibrated using a 0.1 M KCl solution (Wu et al., 1991).

A Schott-Geräte AVS 310 unit equipped with a precalibrated Ubbelohde viscometer having constants of 0.1126 and 0.3099 $\mathrm{mm^2\ s^{-2}}$ was used to measure viscosities. The experimental reproducibility between the duplicate viscosities of all systems was within ±0.4%.

Densities (ρ) were measured with an accuracy of ±0.01% using a single-stem graduated and precalibrated pycnometer (≈9 $\mathrm{cm^3}$) provided with a well-fitted glass stopper to prevent evaporation.

All the measurements were made for $0.3[x\mathrm{KNO_3} + (1 - x)\mathrm{LiNO_3}] + 0.7\mathrm{Cd(NO_3)_2}\cdot 4.37\mathrm{H_2O}$ melt systems as functions of composition ($x = 0.0$ to 1.0 mole fraction) and temperature ($\approx 292.15 \le \mathrm{T/K} \le 363.15$). A Schott-Geräte thermostat type CT-1450 was used to maintain the temperature of the study to ±0.02 K.

Results and Discussion

Measured densities (ρ) for $0.3[x\mathrm{KNO_3} + (1 - x)\mathrm{LiNO_3}] + 0.7\mathrm{Cd(NO_3)_2}\cdot 4.37\mathrm{H_2O}$ systems are presented in Table 1 and are found to be a linear function of temperature at a fixed composition (Table 2). Electrical conductivities (κ), viscosities (η), and molar volumes (*V*) as functions of composition and temperature of the present systems are presented in Tables 3, 4, and 5 respectively.

The temperature dependence of both the electrical conductivity and viscosity is non-Arrhenius (≈21% and

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Table 1. Densities (ρ) of the $0.3[x\mathrm{KNO_3} + (1 - x)\mathrm{LiNO_3}] + 0.7\mathrm{Cd(NO_3)_2{\cdot}4.37H_2O}$ Systems as Functions of Temperature and Composition

T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}
$x = 0.0$		$x = 0.1$		$x = 0.2$		$x = 0.4$	
307.95	2226.1	318.20	2210.9	306.60	2219.6	317.40	2223.8
309.95	2223.5	320.25	2208.4	308.55	2217.0	319.40	2221.2
311.90	2221.2	322.25	2206.0	310.45	2214.7	321.35	2218.8
313.85	2218.6	324.35	2203.5	312.55	2212.2	323.50	2216.3
315.80	2216.4	326.30	2201.4	314.40	2210.0	325.60	2214.1
317.70	2213.9	328.20	2198.9	316.30	2207.5	327.50	2211.6
319.80	2211.4	330.25	2196.4	318.30	2205.0	329.75	2209.1
321.60	2209.1	332.25	2194.1	320.30	2202.7	331.45	2206.8
323.65	2206.2	334.20	2191.3	322.30	2199.9	333.50	2204.0
325.70	2204.1	336.15	2189.2	324.20	2197.7	335.60	2201.8
327.80	2201.8	338.20	2186.8	326.15	2195.4	337.40	2199.5
329.65	2199.5	340.20	2184.5	328.10	2193.1	339.25	2197.2
331.60	2197.4	342.05	2182.5	330.00	2191.0	340.90	2195.1
335.50	2192.6	344.05	2179.9	332.00	2188.5	343.00	2192.6
		346.05	2177.7	334.00	2186.3	345.00	2190.4
		348.05	2175.1	336.00	2183.6	347.10	2187.7
		350.05	2172.9	338.00	2181.4	348.90	2185.5
$x = 0.6$		$x = 0.8$		$x = 1.0$			
307.55	2241.5	306.55	2252.5	314.35	2247.1		
309.55	2238.9	308.65	2249.9	316.45	2244.5		
311.55	2236.5	310.70	2247.5	318.40	2242.3		
313.55	2234.0	312.75	2244.9	320.30	2239.8		
315.35	2231.8	314.75	2242.8	322.45	2237.3		
317.60	2229.3	316.80	2240.2	324.40	2234.9		
319.75	2226.7	318.90	2237.7	326.50	2232.0		
321.80	2224.4	320.90	2235.3	328.45	2229.9		
323.80	2221.5	322.90	2232.5	330.25	2227.5		
325.80	2219.4	324.85	2230.3	332.30	2225.2		
327.75	2217.0	326.75	2227.9	334.30	2223.1		
329.95	2214.7	328.90	2225.6	336.30	2220.5		
331.75	2212.6	330.75	2223.5	338.25	2218.3		
333.75	2210.1	332.80	2220.9	340.20	2215.5		
		334.75	2218.7				
		336.70	2216.0				
		338.75	2213.7				

Table 2. Least-Squares Fitted Values of the Density Equation, $\rho = a - b(T - 273.15)$ for $0.3[x\mathrm{KNO_3} + (1 - x)\mathrm{LiNO_3}] + 0.7\mathrm{Cd(NO_3)_2{\cdot}4.37H_2O}$ Systems

x	a/kg·m^{-3}	b/kg·m^{-3}·K^{-1}	std. dev.
0.0	2268.1 ± 0.3	1.2149 ± 0.0073	0.22
0.1	2264.7 ± 0.2	1.1960 ± 0.0041	0.21
0.2	2260.0 ± 0.2	1.2156 ± 0.0044	0.17
0.4	2277.5 ± 0.2	1.2145 ± 0.0040	0.15
0.6	2282.3 ± 0.3	1.1934 ± 0.0062	0.18
0.8	2292.7 ± 0.2	1.2049 ± 0.0037	0.14
1.0	2297.1 ± 0.3	1.2133 ± 0.0055	0.16

≈15% deviation from the linearity in Arrhenius plots respectively), and the following Vogel−Tammann−Fulcher equation was used to analyze the conductivity and viscosity data.

$$Y = A_y \exp[\pm B_y/(T - T_{0y})] \qquad (1)$$

Here Y refers to either conductivity or viscosity. A_y and B_y are constants, and T_{0y} is the ideal glass transition temperature. The B_y parameter is negative for the electrical conductivity. The computed values of the parameters in eq 1 are presented in Table 6.

Variation of T_{0y} with composition, $x = \mathrm{K^+}/(\mathrm{K^+} + \mathrm{Li^+})$, is illustrated in Figure 1a. T_0 values for the electrical conductivity at all compositions are higher than that of viscosity except at $x = 0.0$. The ideal glass transition temperature for the electrical conductivity is independent of composition up to $x = 0.6$ within the uncertainty limit (Table 6) and then decreases smoothly (Figure 1a), whereas the ideal glass transition temperature for the viscosity decreases up to $x = 0.2$ and then increases up to $x = 0.4$. Beyond $x = 0.4$ mole fraction, T_0 decreases nonlinearly with composition.

Table 3. Values of Electrical Conductivity (κ) for $0.3[x\mathrm{KNO_3} + (1 - x)\ \mathrm{LiNO_3}] + 0.7\mathrm{Cd(NO_3)_2{\cdot}4.37H_2O}$ Systems as Functions of Temperature and Composition

T/K	κ/S·m^{-1}	T/K	κ/S·m^{-1}	T/K	κ/S·m^{-1}
$x = 0.0$		$x = 0.2$		$x = 0.4$	
292.85	0.7654	292.85	0.7844	292.85	0.7864
298.15	1.049	295.45	0.9187	298.15	1.073
303.25	1.358	298.15	1.069	303.25	1.393
307.95	1.686	303.25	1.388	307.95	1.743
313.15	2.101	307.95	1.730	313.15	2.176
317.85	2.521	313.15	2.155	317.85	2.617
323.15	3.036	317.85	2.584	323.15	3.154
327.85	3.538	323.15	3.109	327.85	3.684
333.05	4.139	327.85	3.628	333.05	4.310
337.75	4.725	333.05	4.238	337.75	4.915
343.05	5.432	337.75	4.833	343.05	5.624
347.75	6.100	343.05	5.532	347.75	6.300
353.15	6.869	347.75	6.188	353.15	7.093
357.75	7.568	353.15	6.970	357.75	7.790
362.95	8.379	357.75	7.662	362.95	8.631
		362.95	8.482		
$x = 0.6$		$x = 0.8$		$x = 1.0$	
295.45	0.9274	298.15	1.093	295.45	0.9542
298.15	1.081	303.15	1.424	298.15	1.112
303.15	1.403	307.95	1.782	303.15	1.449
307.95	1.761	313.15	2.231	307.95	1.818
313.15	2.197	317.85	2.686	313.15	2.280
317.85	2.644	323.15	3.241	317.85	2.748
323.15	3.183	327.85	3.783	323.15	3.318
327.85	3.716	333.05	4.429	327.85	3.880
333.05	4.348	337.75	5.053	333.05	4.530
337.75	4.961	343.05	5.785	337.75	5.170
343.05	5.676	347.75	6.477	343.05	5.917
347.75	6.357	353.15	7.294	347.75	6.623
353.15	7.165	357.75	8.012	353.15	7.474
357.75	7.878	362.95	8.869	357.65	8.217
362.95	8.724			362.95	9.097

Table 4. Values of Viscosity (η) for $0.3[x\mathrm{KNO_3} + (1 - x)\mathrm{LiNO_3}] + 0.7\ \mathrm{Cd(NO_3)_2{\cdot}4.37H_2O}$ Systems as Functions of Temperature and Composition

T/K	η/mPa·s	T/K	η/mPa·s	T/K	η/mPa·s	T/K	η/mPa·s
$x = 0.0$		$x = 0.1$		$x = 0.2$		$x = 0.4$	
296.65	141.1	295.15	139.7	298.15	109.3	298.15	117.5
298.15	127.9	298.15	115.0	300.65	93.81	300.65	100.5
303.25	93.44	303.25	84.79	303.25	81.00	303.25	86.43
307.95	71.75	307.95	65.46	307.95	62.81	307.95	66.53
313.15	55.22	313.15	50.56	313.15	48.60	313.15	51.18
317.95	44.28	317.95	40.80	317.95	39.31	317.85	41.28
323.15	35.55	323.15	32.89	323.15	31.69	323.15	33.19
327.95	29.47	327.85	27.39	327.85	26.50	327.85	27.63
333.05	24.39	333.15	22.75	333.05	22.06	333.05	22.92
337.85	20.84	337.85	19.48	337.85	18.90	337.85	19.60
343.05	17.73	343.05	16.60	343.05	16.14	343.05	16.70
347.85	15.46	347.85	14.51	347.75	14.11	347.75	14.57
353.15	13.43	353.15	12.64	353.15	12.25	353.15	12.63
$x = 0.6$		$x = 0.8$		$x = 1.0$			
298.15	121.4	298.15	119.1	298.15	111.6		
301.05	101.1	301.35	97.05	301.35	91.26		
303.25	89.11	303.25	87.02	303.25	82.11		
307.95	68.29	307.95	66.70	307.95	63.17		
313.15	52.33	313.15	51.10	313.15	48.60		
317.95	41.99	317.85	40.98	317.85	39.00		
323.15	33.70	323.15	32.79	323.15	31.25		
327.85	28.21	327.85	27.25	327.85	26.04		
333.05	23.37	333.05	22.56	333.05	21.57		
337.85	19.91	337.85	19.26	337.85	18.44		
343.05	16.92	343.05	16.38	343.05	15.70		
347.75	14.70	347.75	14.28	347.75	13.60		
353.15	12.74	353.15	12.36	353.15	11.79		

Electrical conductivities and viscosities of the present systems also vary nonlinearly with the molar volume, and both the properties have been explained by using the following equation similar to eq 1 derived on the basis of the free volume model:

$$Y = A_{1y} \exp[\pm B_{1y}/(V - V_{oy})] \qquad (2)$$

Table 5. Values of Molar Volume (V) for $0.3[x\mathrm{KNO_3} + (1 - x)\,\mathrm{LiNO_3}] + 0.7\mathrm{Cd(NO_3)_2{\cdot}4.37H_2O}$ Systems as Functions of Temperature and Composition

T/K	$V \times 10^6$/ $\mathrm{m^3{\cdot}mol^{-1}}$	T/K	$V \times 10^6$/ $\mathrm{m^3{\cdot}mol^{-1}}$	T/K	$V \times 10^6$/ $\mathrm{m^3{\cdot}mol^{-1}}$	T/K	$V \times 10^6$/ $\mathrm{m^3{\cdot}mol^{-1}}$
$x = 0.0$		$x = 0.1$		$x = 0.2$		$x = 0.4$	
292.85	107.7	295.15	108.4	292.85	108.9	292.85	108.9
298.15	108.0	298.15	108.6	295.45	109.1	298.15	109.2
303.25	108.3	303.25	108.9	298.15	109.2	303.25	109.6
307.95	108.6	307.95	109.1	303.25	109.6	307.95	109.8
313.15	108.9	313.15	109.4	307.95	109.8	313.15	110.1
317.85	109.2	317.95	109.7	313.15	110.1	317.85	110.4
323.15	109.5	323.15	110.0	317.85	110.4	323.15	110.7
327.85	109.8	327.85	110.3	323.15	110.8	327.85	111.0
333.05	110.1	333.15	110.6	327.85	111.1	333.05	111.3
337.75	110.4	337.85	110.9	333.05	111.4	333.75	111.7
343.05	110.7	343.05	111.2	337.75	111.7	343.05	112.0
347.75	111.0	347.85	111.5	343.05	112.0	347.75	112.3
353.15	111.3	353.15	111.9	347.75	112.3	353.15	112.6
357.75	111.6			353.15	112.6	357.75	112.9
362.95	111.9			357.75	112.9	362.95	113.2
				362.95	113.3		
$x = 0.6$		$x = 0.8$		$x = 1.0$			
295.45	109.7	298.15	110.2	295.45	110.7		
298.15	109.9	303.15	110.5	298.15	110.9		
303.15	110.1	307.95	110.8	303.15	111.2		
307.95	110.4	313.15	111.1	307.95	111.4		
313.15	110.7	317.85	111.4	313.15	111.8		
317.85	111.0	323.15	111.7	317.85	112.0		
323.15	111.3	327.85	112.0	323.15	112.4		
327.85	111.6	333.05	112.3	327.85	112.7		
333.05	111.9	337.75	112.6	333.05	113.0		
337.75	112.2	343.05	112.9	337.75	113.3		
343.05	112.5	347.75	113.2	343.05	113.6		
347.75	112.8	353.15	113.5	347.75	113.9		
353.15	113.1	357.75	113.8	353.15	114.2		
357.75	113.4	362.95	114.2	357.65	114.5		
362.95	113.8			362.95	114.8		

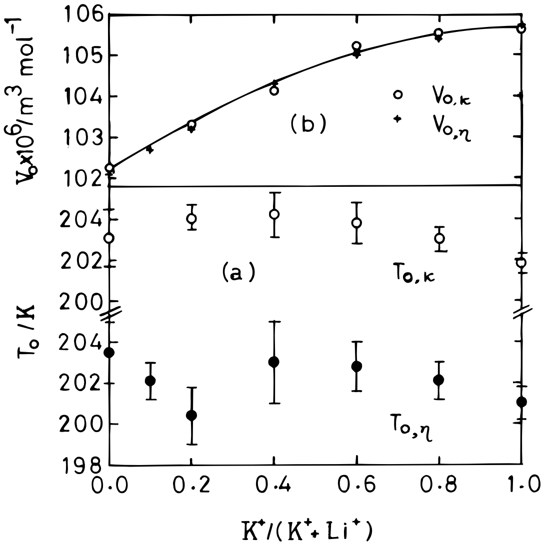

Figure 1. Variation of (a) ideal glass transition temperature, T_o/K, and (b) intrinsic volume, V_0/m^3 mol^{-1}, with $\mathrm{K^+/(K^+ + Li^+)}$ for $0.3[x\mathrm{KNO_3} + (1 - x)\mathrm{LiNO_3}] + 0.7\mathrm{Cd(NO_3)_2{\cdot}4.37H_2O}$ systems.

Y refers either to the conductivity or viscosity. A_{1y} and B_{1y} are constants, and V_{0y} is the intrinsic volume. The least-squares fitted values of A_{1y}, B_{1y}, and V_{0y} are presented in Table 7. For conductivity B_{1y} is negative. The intrinsic volumes, V_0, obtained from the conductivity and viscosity increase nonlinearly (Figure 1b) as the lithium ions are progressively replaced by potassium ions. Such nonlinear variation of V_0 with x is in contrary to what has been observed for other mixed alkali systems (Mahiuddin, 1996; Kalita et al., 1997). In the present system, complex formation may be responsible for the variation of V_0 with $\mathrm{K^+/(K^+ + Li^+)}$ (Figure 1b).

In order to examine the presence of the MAE in the present system, we have illustrated κ and η vs $\mathrm{K^+/(K^+ + Li^+)}$ isotherms in Figures 2 and 3. It is noted that the electrical conductivity isotherms (Figure 2) become slightly nonlinear as the lithium ions are progressively replaced by potassium ions. The MAE in the electrical conductivity isotherms is very small (≈1.0%), and this is contrary to what was observed (≈12.5% negative deviation in the electrical conductivity isotherm at 298.15 K) in $0.45[x\mathrm{LiNO_3} + (1 - x)\mathrm{KNO_3}] + 0.55\mathrm{Ca(NO_3)_2{\cdot}4.09H_2O}$ systems (Easteal, 1981). The absence of the significant mixed alkali effect in the κ isotherms (Figure 2) may be due to the smaller amount of total alkali ion content in comparison to the systems studied by Easteal and Emson (1980) and Easteal (1981).

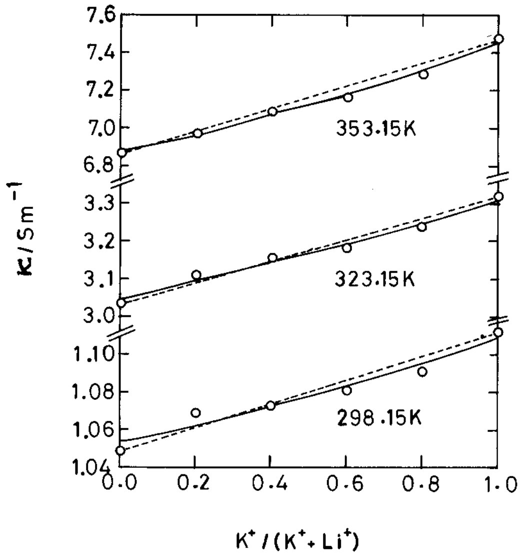

Figure 2. Plots of electrical conductivity isotherms versus $\mathrm{K^+/(K^+ + Li^+)}$ for $0.3[x\mathrm{KNO_3} + (1 - x)\mathrm{LiNO_3}] + 0.7\,\mathrm{Cd(NO_3)_2{\cdot}4.37H_2O}$ systems.

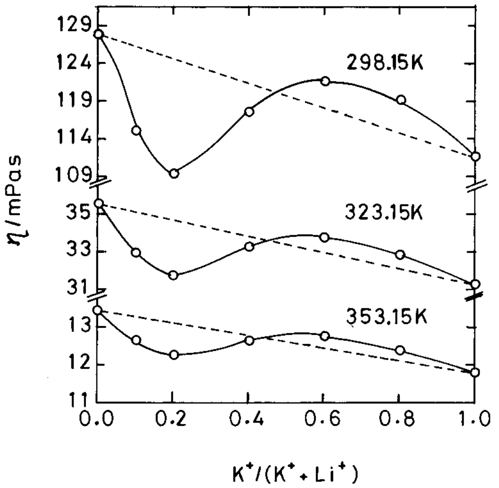

Figure 3. Plots of viscosity isotherms versus $\mathrm{K^+/(K^+ + Li^+)}$ for $0.3[x\mathrm{KNO_3} + (1 - x)\mathrm{LiNO_3}] + 0.7\,\mathrm{Cd(NO_3)_2{\cdot}4.37H_2O}$ systems.

The variation of the viscosity isotherms with $\mathrm{K^+/(K^+ + Li^+)}$ is shown in Figure 3. The deviation of the viscosity isotherms from the additivity is negative (≈7% to 12%) in the $\mathrm{Li^+}$ ion-rich region and is positive (≈2.4% to 4%, which is more than the uncertainties involved in the viscosity data) in the $\mathrm{K^+}$ ion-rich region. Both the positive and negative deviations become pronounced as the temperature decreases, and such deviation may be attributed to the onset of the MAE in the present system.

Although the electrical conductivity isotherm detects the MAE, sometimes they fail to do so. In that case, an alternative method of isofluidity condition (Moynihan, 1979; Sangma et al., 1984) is applied to detect the MAE in

Table 6. Least-Squares Fitted Values of the Parameters of Eq 1 for $0.3[x\mathrm{KNO_3} + (1 - x)\mathrm{LiNO_3}] + 0.7\mathrm{Cd(NO_3)_2{\cdot}4.37H_2O}$ Systems as Functions of Temperature and Composition[a]

x	A_κ/S·m^{-1} (A_η/mPa·s)	B_y/K	T_{0y}/K	std. dev. in ln y
0.0	178.4 ± 8.5	488.8 ± 11.7	203.1 ± 1.4	0.003
	(0.2766 ± 0.0173)	(580.8 ± 15.3)	(203.5 ± 1.5)	(0.002)
0.1	(0.2662 ± 0.0104)	(582.9 ± 9.1)	(202.1 ± 0.9)	(0.001)
0.2	172.9 ± 3.4	478.4 ± 4.9	204.1 ± 0.6	0.002
	(0.2504 ± 0.0140)	(594.2 ± 14.1)	(200.4 ± 1.4)	(0.001)
0.4	179.5 ± 6.2	481.0 ± 8.9	204.2 ± 1.1	0.003
	(0.2666 ± 0.0214)	(579.3 ± 20.1)	(203.0 ± 2.0)	(0.002)
0.6	183.8 ± 5.7	484.3 ± 8.1	203.8 ± 1.0	0.003
	(0.2567 ± 0.0134)	(587.2 ± 12.0)	(202.8 ± 1.2)	(0.003)
0.8	193.2 ± 3.2	491.6 ± 4.7	203.0 ± 0.6	0.005
	(0.2357 ± 0.0125)	(597.6 ± 10.6)	(202.1 ± 0.9)	(0.003)
1.0	210.3 ± 2.9	504.4 ± 4.1	201.8 ± 0.5	0.007
	(0.2229 ± 0.0100)	(603.9 ± 8.1)	(201.0 ± 0.8)	(0.002)

[a] Values for the viscosity are given in parentheses.

Table 7. Least-Squares Fitted Values of the Parameters of Eq 2 for $0.3[x\mathrm{KNO_3} + (1 - x)\mathrm{LiNO_3}] + 0.7\mathrm{Cd(NO_3)_2{\cdot}4.37H_2O}$ Systems as Functions of Temperature And Composition[a]

x	$A_{1\kappa}$/S·m^{-1} ($A_{1\eta}$/mPa·s)	$B_{1y} \times 10^5$/m^3·mol^{-1}	V_{0y}/m^3·mol^{-1}	std. dev. in ln y
0.0	184.0±12.0	2.988±0.104	102.2±0.1	0.008
	(0.2418 ± 0.0179)	(3.696 ± 0.103)	(102.1 ± 0.1)	(0.005)
0.1	(0.2270 ± 0.0543)	(3.650 ± 0.303)	(102.7 ± 0.3)	(0.031)
0.2	183.5 ± 28.8	3.051 ± 0.249	103.3 ± 0.4	0.025
	(0.2565 ± 0.0363)	(3.647 ± 0.196)	(103.2 ± 0.3)	(0.028)
0.4	123.4 ± 14.9	2.431 ± 0.154	104.1 ± 0.2	0.022
	(0.4941 ± 0.1127)	(2.702 ± 0.256)	(104.3 ± 0.3)	(0.029)
0.6	104.0 ± 11.3	2.116 ± 0.148	105.2 ± 0.2	0.023
	(0.4572 ± 0.0701)	(2.709 ± 0.176)	(105.0 ± 0.2)	(0.023)
0.8	107.7 ± 12.5	2.168 ± 0.142	105.5 ± 0.2	0.012
	(0.04721 ± 0.0625)	(2.666 ± 0.179)	(105.4 ± 0.2)	(0.015)
1.0	150.0 ± 16.2	2.586 ± 0.154	105.6 ± 0.2	0.021
	(0.3635 ± 0.0682)	(2.974 ± 0.281)	(105.7 ± 0.3)	(0.027)

[a] Values for the viscosity are given in parentheses.

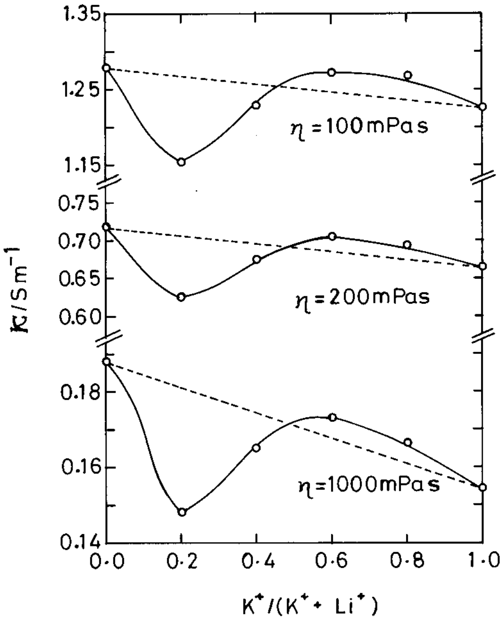

Figure 4. Plots of electrical conductivity versus $\mathrm{K^+/(K^+ + Li^+)}$ under isoviscosity conditions for $0.3[x\mathrm{KNO_3} + (1 - x)\mathrm{LiNO_3}] + 0.7\mathrm{Cd(NO_3)_2{\cdot}4.37H_2O}$ systems.

ternary systems containing hydrate melt. Accordingly, the electrical conductivities under the isoviscosity condition, both within and outside the experimental viscosity range, were calculated by using eq 1 and the least-squares fitted values of A_y, B_y, and T_{0y} parameters (Table 6). From Figure 4 it is apparent that the nature of variation of κ vs $\mathrm{K^+/(K^+ + Li^+)}$ under the isoviscosity condition is similar to that of the viscosity isotherms (Figure 3).

The magnitude of the negative deviation (≈7% to 18%) in the $\mathrm{Li^+}$ ion-rich region and the positive deviation (≈2.4% to 4%) in the $\mathrm{K^+}$ ion-rich region (Figures 3 and 4) increase as the viscosity of the system increases. Such deviation in the present system, particularly in the $\mathrm{Li^+}$ ion-rich region, is higher than that of the $\mathrm{Na^+}$–$\mathrm{K^+}$ mixed alkali system in hydrate melt and molecular liquid media (Sangma et al., 1984; Islam and Ismail, 1990; Mahiuddin, 1994), which may be due to the higher difference in the cation field strength proposed by Dietzel (1983). In general the anion polarization model (APM) (Moynihan and Laity, 1964; Moynihan, 1971) has been used to explain the MAE. The nature of deviation in the present system may be of different origin. In our earlier sodium thiocyanate–potassium thiocyanate–acetamide systems (Mahiuddin, 1996), we have reported both the negative deviation (≈27%) in the $\mathrm{Na^+}$ ion-rich region and the positive deviation (≈4.6%) in the $\mathrm{K^+}$ ion-rich region but not together as found in the present system. The negative deviation in the $\mathrm{Li^+}$ ion-rich region (Figures 3 and 4) may be due to the resultant effect of greater polarization of $\mathrm{NO_3^-}$ ion on the $\mathrm{Li^+}$ ion when the medium contains both $\mathrm{K^+}$ and $\mathrm{Li^+}$ ions and the ionic complex of cadmium formed (Kanno, 1986), whereas the positive deviation in the $\mathrm{K^+}$ ion-rich region may be governed by the lesser polarization of $\mathrm{NO_3^-}$ ion on the $\mathrm{K^+}$ ion.

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