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Dynamic Viscosities of KI or NH_4I in Methanol and NH_4I in Ethanol at Several Temperatures and 0.1 MPa

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Viscosities and densities have been determined for some binary strong electrolyte solutions—KI + methanol, NH_4I + methanol and NH_4I + ethanol—at (298.15, 303.15, 308.15, and 313.15) K and 0.1 MPa. The viscosity data have been analyzed using the three-parameter Jones−Dole equation (Kaminsky, M. Ion−solvent interaction and the viscosity of strong electrolyte solutions. *Discuss. Faraday Soc.* **1957**, *24*, 171−179), and the *A, B*, and *D* parameters have been calculated. A Debye−Hückel model for calculating the viscosity proposed by Esteves et al. (Esteves, M.; Cardoso, M.; Barcia, O. A Debye−Hückel model for calculating the viscosity of binary strong electrolyte solutions. *Ind. Eng. Chem. Res.* **2001**, *40*, 5021−5028. Esteves, M.; Cardoso, M.; Barcia, O. A Debye−Hückel Model for Calculating the Viscosity of Binary Strong Electrolyte Solutions at Different Temperatures. *Ind. Eng. Chem. Res.* **2002**, *41*, 5109−5113) has been used to correlate the experimental data.

Introduction

Information about physical properties such as the density and viscosity of liquid mixtures is necessary in chemical engineering applications such as designs involving fluid-flow, mass-transfer, and heat-transfer operations. As an extension of our work on the determination of the dynamic viscosity of binary systems, we present the experimental dynamic viscosity and density of binary systems KI + methanol and NH_4I + methanol or ethanol at (298.15, 303.15, 308.15, and 313.15) K. The Jones−Dole equation[1] has been used to analyze the viscosity data, and the model developed by Esteves et al.[2,3] for binary strong electrolyte solutions has been used to correlate the experimental dynamic viscosity data.

Experimental Section

Chemicals. Ammonium iodide (>99.5%) was supplied by Fluka, potassium iodide (>99.5%) was supplied by Riedel-deHäen, and methanol (>99.8%) and ethanol (>99.9%) were supplied by Merck. Methanol and ethanol were degassed by ultrasound, dried over molecular sieves (type 4 Å, Aldrich), and kept in inert argon with a maximum water content of 2×10^{-6} by mass fraction. The density and viscosity of the solvents were compared with published values at 298.15 K in Table 1.

Apparatus and Procedure. Samples were prepared by mass using a Mettler AX-205 Delta Range balance with a precision of $\pm 10^{-5}$ g. Densities of the pure liquids and mixtures were measured using an Anton Paar DSA-45 digital vibrating-tube densimeter. The uncertainty in the density mesurements is $\pm 10^{-5}$ g·cm^{-3}.

The kinematic viscosities were determined by using a Lauda PSV1 automatic viscosimeter with two Ubbelhode capillary microviscosimeters with diameters of 0.4×10^{-3} and 0.53×10^{-3} m. The gravity fall is the principle of measurement on which this viscosimeter is based. The capillary is maintained in a D20KP Lauda thermostat with a resolution of 0.01 K. The capillaries are calibrated and certified by the company that supplies us. The uncertainty of the capillary diameter is ±0.005 mm. The equipment has a PSV1 control unit that is a PC-controlled instrument for the precise measurement of fall time, using standardized glass capillaries, with an accuracy of 0.01 s. The uncertainty of the viscosimeter is better than 0.001 mPa·s.

Table 1. Comparison of Density, ρ, and Viscosity, η, with Literature Data for Pure Components at T = 298.15 K and P = 0.1 MPa

	ρ/g·cm^{-3}		η/mPa·s	
component	experimental	literature	experimental	literature
ethanol	0.7852	0.78509[b]	1.082	1.0826[b]
methanol	0.7862	0.78664[a,b]	0.545	0.545[b] 0.5513[a]

[a] Riddick et al.[7] [b] Das et al.[8]

Results and Discussion

The experimental densities, apparent molar volumes, and viscosities of the binary systems KI + methanol, NH_4I + methanol, and NH_4I + ethanol at (298.15, 303.15, 308.15, and 313.15) K and 0.1 MPa are given in Tables 2 to 4.

The apparent molar volumes V_ϕ were determined from the solution densities using the following equation:[4]

$$V_\Phi = \frac{M_w}{\rho} - 1000\frac{(\rho - \rho_0)}{(\rho\rho_0 m)} \tag{1}$$

where M_w is the molecular weight of the solute, m is the

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Table 2. Densities, ρ, Apparent Molar Volumes, V_ϕ, and Dynamic Viscosities, η, of KI (1) + Methanol (2) at (298.15, 303.15, 308.15, and 313.15) K and 0.1 MPa

c/mol·L^{-1}	ρ/g·cm^3	V_ϕ/cm·mol	η/mPa·s	c/mol·L^{-1}	ρ/g·cm^3	V_ϕ/cm^3·mol	η/mPa·s
	298.15 K				303.15 K		
0.0906	0.8008	13.32	0.578	0.0901	0.7961	13.17	0.539
0.1458	0.8090	16.18	0.598	0.1449	0.8043	15.77	0.558
0.1806	0.8143	16.50	0.609	0.1795	0.8096	16.01	0.568
0.2451	0.8243	16.05	0.628	0.2437	0.8195	15.47	0.587
0.3767	0.8453	13.24	0.665	0.3745	0.8406	12.58	0.620
0.4151	0.8516	12.40	0.677	0.4127	0.8468	11.75	0.631
0.4787	0.8622	10.39	0.695	0.4760	0.8575	9.72	0.653
0.5381	0.8724	8.53	0.724	0.5350	0.8676	7.81	0.664
0.6140	0.8854	6.78	0.737	0.6106	0.8805	6.07	0.685
0.6541	0.8927	5.12	0.750	0.6505	0.8878	4.37	0.697
	308.15 K				313.15 K		
0.0895	0.7913	13.20	0.504	0.1432	0.7948	29.41	0.489
0.1441	0.7996	15.47	0.522	0.1774	0.8001	26.66	0.498
0.1785	0.8049	15.59	0.532	0.2409	0.8100	22.86	0.513
0.2423	0.8148	14.95	0.548	0.3704	0.8311	16.44	0.543
0.3724	0.8358	11.93	0.580	0.4081	0.8372	15.38	0.552
0.4104	0.8420	11.08	0.590	0.4707	0.8478	12.62	0.572
0.4733	0.8527	9.02	0.615	0.5291	0.8580	10.19	0.580
0.5321	0.8628	7.09	0.623	0.6040	0.8708	7.95	0.598
0.6073	0.8757	5.33	0.639	0.6435	0.8781	6.01	0.608
0.6470	0.8830	3.62	0.651				

Table 3. Densities, ρ, Apparent Molar Volumes, V_ϕ, and Dynamic Viscosities, η, of NH_4I (1) + Methanol (2) at (298.15, 303.15, 308.15, and 313.15) K and 0.1 MPa

c/mol·L^{-1}	ρ/g·cm^3	V_ϕ/cm^3·mol	η/mPa·s	c/mol·L^{-1}	ρ/g·cm^3	V_ϕ/cm^3·mol	η/mPa·s
	298.15 K				303.15 K		
0.1696	0.8072	29.06	0.597	0.1686	0.8026	28.56	0.557
0.3281	0.8263	29.52	0.628	0.3262	0.8216	29.05	0.586
0.4765	0.8454	26.33	0.674	0.4739	0.8408	25.63	0.628
0.5862	0.8594	25.27	0.688	0.5810	0.8545	24.60	0.648
0.5841	0.8591	25.39	0.692	0.7443	0.8772	20.56	0.688
0.7482	0.8818	21.31	0.737	0.8692	0.8948	18.19	0.719
0.8737	0.8994	18.96	0.771	0.9897	0.9123	15.83	0.749
0.9947	0.9169	16.61	0.802	1.0993	0.9288	13.34	0.781
1.1047	0.93334	14.14	0.836	1.2031	0.9446	11.23	0.809
1.2089	0.9492	12.05	0.865	1.3273	0.9638	8.94	0.847
1.3337	0.9684	9.76	0.903	1.4099	0.9769	7.29	0.868
1.4165	0.9815	8.12	0.930	1.500	0.9916	5.42	0.898
1.5069	0.9962	6.25	0.960				
	308.15 K				313.15 K		
0.1676	0.7979	28.11	0.522	0.1667	0.7931	39.84	0.490
0.3018	0.8139	29.53	0.540	0.3001	0.8092	35.69	0.506
0.4712	0.8361	24.93	0.587	0.4686	0.8314	28.49	0.551
0.5799	0.8501	23.82	0.600	0.5767	0.8454	26.56	0.563
0.7404	0.8726	19.79	0.644	0.7364	0.8679	21.71	0.604
0.8647	0.8902	17.40	0.682	0.8602	0.8855	18.91	0.631
0.9847	0.9076	15.02	0.701	0.9797	0.9030	16.23	0.658
1.0939	0.9243	12.45	0.729	1.0889	0.9200	13.03	0.685
1.1972	0.9400	10.40	0.756	1.1913	0.9354	11.22	0.710
1.3210	0.9592	8.08	0.789	1.3147	0.9246	8.73	0.741
1.4032	0.9723	6.44	0.813	1.3966	0.9677	7.00	0.763
1.4930	0.9870	4.56	0.840	1.4861	0.9824	5.03	0.788

molality, and ρ_0 and ρ are the densities of the solvent and the solution, respectively.

The molalities of the solution can be calculated from the molarities c (mol·L^{-1}) using the equation

$$m = \frac{1}{(\rho/c) - M_w/1000} \tag{2}$$

For all of these binary systems, the apparent molar volume decreases with increasing concentration and shows a very small temperature effect in the range of 298.15 to 313.15 K. These results suggest that the ion−solvent interactions decrease with increasing electrolyte concentration.

The Jones−Dole equation can be used to analyze the viscosity data of electrolyte solutions. This equation is valid up to a concentration of 0.1 M. For higher concentrations, a quadratic term is added:[1]

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc + Dc^2 \tag{3}$$

where η and η_0 are the viscosities of the mixture and the pure solvent, respectively, c is the salt concentration (mol·L^{-1}), and A, B, and D are the parameters. Values of parameters A, B, and D estimated for this systems are summarized in Table 5. Using these parameters, we can calculate the relative viscosity of these systems with good agreement.

The experimental viscosities have been correlated using the model proposed by Esteves et al.[2,3] based on the absolute rate theory of Eyring[5,6] and a Debye−Hückel-type

Table 4. Densities, ρ, Apparent Molar Volumes, V_ϕ, and Dynamic Viscosities, η, of NH_4I (1) + Ethanol (2) at (298.15, 303.15, 308.15, and 313.15) K and 0.1 MPa

c/mol·L^{-1}	ρ/g·cm^3	V_ϕ/cm^3·mol	η/mPa·s	c/mol·L^{-1}	ρ/g·cm^3	V_ϕ/cm^3·mol	η/mPa·s
298.15 K				303.15 K			
0.1638	0.8041	36.39	1.229	0.1629	0.7998	34.90	1.120
0.2289	0.8117	35.72	1.275	0.2276	0.8074	34.52	1.161
0.3302	0.8239	34.25	1.350	0.3285	0.8196	33.18	1.225
0.4015	0.8327	32.78	1.414	0.3994	0.8284	31.79	1.284
0.4696	0.8411	31.71	1.495	0.4673	0.8369	30.60	1.359
0.6094	0.8594	28.31	1.557	0.6064	0.8551	27.42	1.413
0.6694	0.8670	27.67	1.598	0.6661	0.8627	26.81	1.454
0.7343	0.8758	26.08	1.663	0.7307	0.8716	25.24	1.499
0.8676	0.8945	22.83	1.770	0.8635	0.8902	22.02	1.599
0.9720	0.9089	21.17	1.839	0.9674	0.9047	20.36	1.674
308.15 K				313.15 K			
0.1620	0.7955	34.09	1.048	0.1611	0.7911	33.14	.935
0.2264	0.8031	33.75	1.059	0.2252	0.7988	32.85	.968
0.3268	0.8153	32.41	1.117	0.3251	0.8110	31.55	1.020
0.3974	0.8241	31.04	1.165	0.3952	0.8197	30.22	1.062
0.4658	0.8342	25.74	1.241	0.4634	0.8293	26.52	1.100
0.6033	0.8508	26.69	1.287	0.6003	0.8465	25.89	1.175
0.6628	0.8584	26.09	1.327	0.6595	0.8541	25.29	1.226
0.7271	0.8673	24.51	1.365	0.7235	0.8630	23.71	1.246
0.8593	0.8859	21.29	1.459	0.8551	0.8816	20.50	1.324
0.9628	0.9004	19.63	1.544	0.9582	0.8961	18.84	1.388

Table 5. *A*, *B*, and *D* Coefficients of the Jones−Dole Equation

system	T/K	A/L$^{1/2}$·mol$^{-1/2}$	B/L·mol^{-1}	D/L^2·mol^2
IK + methanol	298.15	0.0679	0.4663	0.0317
	303.15	−0.0109	0.6351	−0.1084
	308.15	0.0015	0.6293	−0.1141
	313.15	−0.0014	0.6034	−0.0923
NH_4I + methanol	298.15	0.1024	0.2758	0.0971
	303.15	0.0987	0.2878	0.0938
	308.15	0.0684	0.3384	0.0774
	313.15	0.0991	0.2924	0.0973
NH_4I + ethanol	298.15	0.0478	0.6707	−0.0094
	303.15	0.0711	0.6161	0.0186
	308.15	0.2327	0.2703	0.2261
	313.15	0.0748	0.5609	0.0656

expression for calculating the excess free energy of activation of the viscous flow. The ratio between the viscosity of an electrolyte solution at a given temperature T, pressure P, solvent chemical potential μ_1, and moles of the solute species n_i and the viscosity of an ideal dilute solution at the same T, P, n_i, and μ_1 as the real solution can be written as follows:

$$\frac{\eta-\eta_1}{\eta_{\mathrm{id}}-\eta_1} = \left(\frac{\sum_{i=1}^{N_\mathrm{s}} c_i}{\sum_{i=1}^{N_\mathrm{s}} c_{i,\mathrm{id}}}\right)\exp\left(\frac{\Delta G_\mathrm{E}^{\ddagger}}{RT}\right) \tag{4}$$

where η_1 is the pure solvent dynamic viscosity, N_s is the number of solute species, c_i and $c_{i,\mathrm{id}}$ are the molar concentrations of the solute species of the solution and of the ideal dilute solution, respectively, R is the gas constant, T is the absolute temperature, and $\Delta G_\mathrm{E}^{\ddagger}$ is the excess free energy of activation of the electrolyte solution per mole of solute species.

The ideal dilute solution viscosity can be calculated by the following expression:

$$\eta_{\mathrm{id}} = \eta_1\left(1 + K\sum_{i=1}^{N_\mathrm{s}} c_{i,\mathrm{id}}\right) \tag{5}$$

where K was taken as an empirical adjustable parameter.

The excess free energy of activation, $\Delta G_\mathrm{E}^{\ddagger}$, takes into account the electrostatic interactions of the ionic solute species in a continuous solvent

$$\Delta G_\mathrm{E}^{\ddagger} = \Delta G_\mathrm{E}^{\ddagger,\mathrm{DH}} + \Delta G_\mathrm{E}^{\ddagger,\mathrm{G}} \tag{6}$$

where $\Delta G_\mathrm{E}^{\ddagger,\mathrm{DH}}$ is the contribution calculated by means of the Debye−Hückel primitive model and $\Delta G_\mathrm{E}^{\ddagger,\mathrm{G}}$ represents a contribution related to a Guggenheim-type expression. For a binary mixture of one electrolyte plus one solvent, one can write

$$\Delta G_\mathrm{E}^{\ddagger,\mathrm{DH}} = -\frac{4.6581 \times 10^7 I^{3/2}}{D^{3/2}T^{1/2}\nu c_2}\tau(\kappa a) \tag{7}$$

with

$$\tau(\kappa a) = 3(\kappa a)^{-3}\left[\ln(1+\kappa a) - \kappa a + \frac{(\kappa a)^2}{2}\right] \tag{8}$$

and

$$\Delta G_\mathrm{E}^{\ddagger,\mathrm{G}} = \frac{RTFI^2}{\nu c_2} \tag{9}$$

where I is the ionic strength of the solution, κ is the inverse of the Debye length, a is the distance of closest approach of two ionic species taken as the arithmetic mean of their radii, D is the dielectric constant of the solvent, ν is the sum of the stoichiometric coefficients of the cation and anion of a given electrolyte ($\nu = \nu_+ + \nu_-$), c_2 is the electrolyte concentration, and F is taken as an empirical adjustable parameter.

The following temperature dependence expressions have been used to calculate correlation parameters K and F:

$$K(T) = P_1^K + P_2^K(T - T_\mathrm{R}) \tag{10}$$

$$F(T) = P_1^F + P_2^F\left(\frac{1}{T} - \frac{1}{T_\mathrm{R}}\right) + P_3^F\ln\left(\frac{T}{T_\mathrm{R}}\right) \tag{11}$$

where T is the absolute temperature in K, T_R is a reference

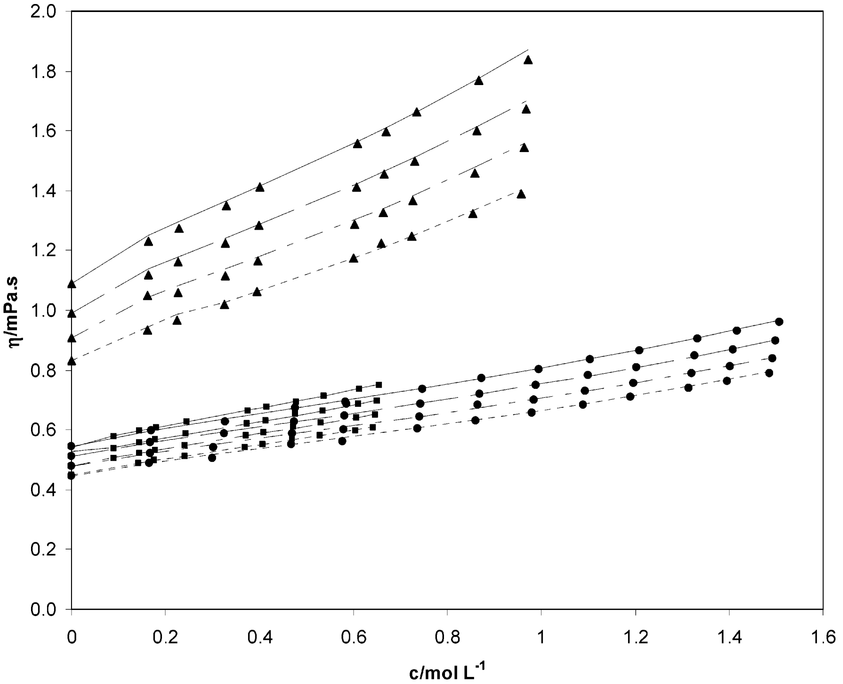

Figure 1. Comparison between experimental and calculated dynamic viscosity at 0.1 MPa. Experimental data: ■, KI + methanol; ●, NH_4I + methanol; and ▲, NH_4I + ethanol. Calculated values: —, 298.15 K; – –, 303.15 K; – - –, 308.15 K; and - - -, 313.15 K.

Table 6. Correlation Parameters

	P_1^K	P_2^K	P_1^K	P_2^F	P_3^F
system	$L\cdot mol^{-1}$	$L\cdot mol^{-1}\cdot K^{-1}$	$L\cdot mol^{-1}$	$L\cdot K\cdot mol^{-1}$	$L\cdot mol^{-1}$
KI + methanol	0.6457	0.00303	1.0238	1055.01	2.27
NH_4I + methanol	0.7558	0.00182	0.5039	4513.66	15.72
NH_4I + ethanol	1.2418	$4.81\cdot10^{-5}$	1.0965	1051.99	6.39

Table 7. Mean Relative Standard Deviation for Binary Systems

	MRSD			
system	298.15 K	303.15 K	308.15 K	313.15 K
KI + methanol	0.0021	0.0042	0.0056	0.0042
NH_4I + methanol	0.0036	0.0041	0.0053	0.0042
NH_4I + ethanol	0.0065	0.0050	0.0060	0.0075

temperature, taken as 298.15 K, and P_1^K, P_2^K, P_1^F, P_2^F, and P_3^F are the adjustable parameters.

The objective function used in the determination of model parameters was

$$\mathrm{OF} = \sum_{i=1}^{N_D} (\eta_i^{\mathrm{calcd}} - \eta_i^{\mathrm{exptl}})^2 \tag{12}$$

where N_D is the number of experimental data and η_i^{calcd} and η_i^{exptl} are, respectively, the calculated and experimental values of the dynamic viscosity.

The calculated viscosity values are compared with the experimental values by means of the mean relative standard deviation

$$\mathrm{MRSD} = \left(\frac{1}{N_D}\sum_{i=1}^{N_D}\left(\frac{\eta_i^{\mathrm{calcd}} - \eta_i^{\mathrm{exptl}}}{\eta_i^{\mathrm{exptl}}}\right)^2\right)^{1/2} \tag{13}$$

Table 6 shows the correlation parameters for the systems, and Table 7 shows the correlation results. Figure 1 shows the experimental data and correlation curves for the binary systems. It can be seen that the model correlates the experimental data with good agreement.

Conclusions

In this paper, we have determined the experimental densities and dynamic viscosities of the binary systems KI + methanol, NH_4I + methanol, and NH_4I + ethanol at (298.15, 303.15, 303.15, and 313.15) K.

Jones–Dole parameters *A*, *B*, and *D* have been calculated for these systems.

The model developed by Esteves et al.[2,3] has been used to correlate the experimental dynamic viscosity data. In view of these results, we can say that the model can adequately correlate the viscosities of these binary mixtures.

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