J. Chem. Eng. Data **1999,** *44*, 1091−1096

Density and Viscosity in Electrolyte Solutions Based on Binary Solvents

Sergei G. Korotkov, Lina M. Kuznetsova, and Elena A. Ovchinnikova*

Departement of Chemistry, Saratov State University, 410071 Saratov, Russia

---

A viscometric and volumetric study was performed on electrolyte solutions containing $LiClO_4$ and the redox couple NaI and I_2 in six aprotic binary solvents composed of mixtures of acetonitrile, *N*,*N*-dimethylformamide, methyl Ethyl ketone, and ethyl acetate over the temperature range 253.15 K to 313.15 K. A formula is proposed to describe the results of these (their deviation) binary (quasibinary) systems as a power function of composition and temperature.

Introduction

Systems containing a redox couple I_3^-/I^-, a salt $LiClO_4$, and a solvent are used in molecular−electronic diffusional sensors (MEDS). The use of nonaqueous solvents has considerably expanded the working temperature range of MEDS. As a rule, a better electrochemical performance is characterized by systems with a solvent which has a low viscosity and a high ionizing ability. Among individual solvents, it is difficult to find one that meets all the requirements, and mixed binary solvents are widely used. By varying the composition of an electrolyte in a solvent, one can finely tune both chemical (donor−acceptor interactions, ion diffusion, equilibrium constants) and physical (density, viscosity, permittivity, etc.) properties of the medium (Fialkov, 1990).

Experimental Section

Materials. Acetonitrile (AN) (chemicaly pure, mass purity 99.0%), *N*,*N*-dimethylformamide (DMFA) (chemicaly pure, mass purity 99.7%), and ethyl acetate (EA) (chemicaly pure, mass purity 99.1%) were purchased from Reakhim (Russia), and methyl ethyl ketone (MEK) (purum, mass purity 99.0%) was from Renal (Hungary). Solvents were purified, dried as described by Ford and Gordon (1972), and then degassed under vacuum. The water content was less than 0.003 mass % in the liquids from analysis by the Karl Fischer method.

Sodium iodide dihydrate ($NaI{\cdot}2H_2O$), lithium perchlorate ($LiClO_4$), and iodine (I_2) were purchased from Reakhim (Russia). All the salts (Analar) were twice recrystallized from doubly distilled water and dried under vacuum (0.13 kPa) with gradual heating to 453.15 K until constant mass was reached. Thermogravimetric analysis showed the absence of hydrate peaks. Iodine (extra pure) was used without further purification.

Solutions were prepared gravimetrically and contained 0.5 $mol{\cdot}L^{-1}$ $LiClO_4$, 2.76×10^{-2} $mol{\cdot}L^{-1}$ NaI, and 5.51×10^{-3} $mol{\cdot}L^{-1}$ I_2 (molar concentration at 298.15 K). Solutions containing binary solvent were prepared gravimetrically by mixing of solutions containing individual solvents. The solutions were kept in amber-colored bottles for use in the experiments. All the chemicals were stored in a desiccator filled with silica gel.

Apparatus and Procedure. The densities of the solutions were measured with a pycnometer. The kinematic viscosities of the solutions were measured by means of an Ubbelhode viscometer. The efflux time was measured with a stopwatch to 0.1 s. The temperature coefficient of the viscometer was determined as follows. The viscosity of the liquid mixtures can be calculated at fixed temperature as

$$\eta = k{\cdot}t{\cdot}\rho \qquad (1)$$

or

$$\nu = k{\cdot}t \qquad (2)$$

where *k* is the viscometer constant, *t* is the efflux time of a standard liquid (used doubly distilled water and acetone (Handbook of Chemistry, 1962; Karapetian and Eychis, 1989)), ρ is the density, η, ν are respectively the dynamic and kinematic viscosities of the standard liquid. (2) for polytherm can be written as

$$\ln k = \ln \nu - \ln t \qquad (3)$$

The temperature dependences of the viscosity and the efflux time have behavior of the Arrhenius type, that is

$$\ln \nu = A + \frac{B}{T} \qquad (4)$$

$$\ln t = C + \frac{D}{T} \qquad (5)$$

Having substituted eqs 4 and 5 into eq 3, a final equation for the temperature coefficient of the viscometer is obtained

$$\ln k = A - C + \frac{B - D}{T} \qquad (6)$$

The temperature coefficient of the pycnometer

$$V(T) = \frac{m(T)}{\rho(T)} \qquad (7)$$

where *m(T)* and *ρ(T)* are analytical expressions for the mass and the density of a standard liquid as a function of temperature.

Measurements were carried out at 253.15, 263.15, 273.15, 298.15, and 313.15 K with an accuracy of 0.1 K. The

---

* Corresponding author. E-mail: box@vnipigaz.saratov.su.

10.1021/je980271d CCC: $18.00 © 1999 American Chemical Society
Published on Web 08/21/1999

Table 1. Experimental Densities ρ and Molecular Weight M_{add} of Solutions Containing 0.5 mol·L^{-1} $LiClO_4$, 2.76 × 10^{-2} mol·L^{-1} NaI, and 5.51 × 10^{-3} mol·L^{-1} I_2 (concentration at 298.15 K)

Acetonitrile (1) + *N*,*N*-Dimethylformamide (2)

	ρ/(g·cm^{-3})					
T/K	$M_{add} = 42.944$ $x_1 = 1$	$M_{add} = 47.425$ $x_1 = 0.8583$	$M_{add} = 52.866$ $x_1 = 0.6862$	$M_{add} = 59.014$ $x_1 = 0.4917$	$M_{add} = 66.371$ $x_1 = 0.2589$	$M_{add} = 74.577$ $x_1 = 0$
253.15	0.8698	0.8947	0.928	0.9595	0.9896	1.0234
263.15	0.8593	0.8900	0.9213	0.9519	0.9863	1.0161
273.15	0.8483	0.8782	0.9115	0.9447	0.9770	1.0065
298.15	0.8228	0.8550	0.8883	0.9216	0.9534	0.9834
313.15	0.8075	0.8383	0.8735	0.9058	0.9401	0.9704

Acetonitrile (1) + Ethyl Acetate (2)

	ρ/(g·cm^{-3})					
T/K	$M_{add} = 42.944$ $x_1 = 1$	$M_{add} = 48.622$ $x_1 = 0.8771$	$M_{add} = 55.609$ $x_1 = 0.7259$	$M_{add} = 64.671$ $x_1 = 0.5298$	$M_{add} = 76.131$ $x_1 = 0.2817$	$M_{add} = 89.147$ $x_1 = 0$
253.15	0.8698	0.8941	0.9246	0.9492	0.9697	0.9907
263.15	0.8593	0.8896	0.9166	0.9428	0.9642	0.9839
273.15	0.8483	0.8776	0.9040	0.9320	0.9535	0.9726
298.15	0.8228	0.8527	0.8789	0.9034	0.9266	0.9439
313.15	0.8075	0.8362	0.8628	0.8872	0.9084	0.9271

Ethyl Acetate (1) + *N*,*N*-Dimethylformamide (2)

	ρ/(g·cm^{-3})					
T/K	$M_{add} = 89.147$ $x_1 = 1$	$M_{add} = 85.200$ $x_1 = 0.7295$	$M_{add} = 82.536$ $x_1 = 0.5468$	$M_{add} = 79.596$ $x_1 = 0.3453$	$M_{add} = 76.861$ $x_1 = 0.1579$	$M_{add} = 74.557$ $x_1 = 0$
253.15	0.9907	1.0002	1.0081	1.0135	1.0172	1.0234
263.15	0.9839	0.9944	1.0026	1.0074	1.0118	1.0161
273.15	0.9726	0.9824	0.9907	0.9968	1.0027	1.0065
298.15	0.9439	0.9557	0.9649	0.9725	0.9788	0.9834
313.15	0.9271	0.9399	0.9492	0.9573	0.9634	0.9704

Methylethyl ketone (1) + Acetonitrile (2)

	ρ/(g·cm^{-3})					
T/K	$M_{add} = 73.845$ $x_1 = 1$	$M_{add} = 68.721$ $x_1 = 0.8342$	$M_{add} = 64.756$ $x_1 = 0.7059$	$M_{add} = 58.942$ $x_1 = 0.5177$	$M_{add} = 51.717$ $x_1 = 0.2839$	$M_{add} = 47.311$ $x_1 = 0.1413$
253.15	0.8922	0.8844	0.8866	0.8820	0.8746	0.8704
263.15	0.8845	0.8822	0.8817	0.8766	0.8703	0.8657
273.15	0.8747	0.8731	0.87	0.8646	0.8592	0.855
298.15	0.8496	0.8481	0.8466	0.8404	0.8339	0.8285
313.15	0.8337	0.8321	0.8307	0.8257	0.8191	0.8129

Methylethyl ketone (1) + *N*,*N*-Dimethylformamide (2)

	ρ/(g·cm^{-3})					
T/K	$M_{add} = 73.845$ $x_1 = 1$	$M_{add} = 73.929$ $x_1 = 0.8820$	$M_{add} = 74.011$ $x_1 = 0.7660$	$M_{add} = 74.147$ $x_1 = 0.5756$	$M_{add} = 74.289$ $x_1 = 0.3764$	$M_{add} = 74.434$ $x_1 = 0.1735$
253.15	0.8922	0.9039	0.9181	0.9444	0.9707	0.9993
263.15	0.8845	0.8986	0.9133	0.939	0.9644	0.9938
273.15	0.8747	0.8888	0.9016	0.9288	0.9547	0.9839
298.15	0.8496	0.8655	0.8795	0.9044	0.9324	0.9608
313.15	0.8337	0.8498	0.8648	0.8900	0.9182	0.9469

Methyl Ethyl Ketone (1) + Ethyl Acetate (2)

	ρ/(g·cm^{-3})					
T/K	$M_{add} = 73.845$ $x_1 = 1$	$M_{add} = 75.277$ $x_1 = 0.8696$	$M_{add} = 77.244$ $x_1 = 0.7779$	$M_{add} = 79.960$ $x_1 = 0.6004$	$M_{add} = 82.725$ $x_1 = 0.4197$	$M_{add} = 85.843$ $x_1 = 0.2160$
253.15	0.8922	0.9048	0.9208	0.9341	0.9526	0.9706
263.15	0.8845	0.8988	0.9132	0.9289	0.9464	0.9662
273.15	0.8747	0.8882	0.9017	0.9185	0.9355	0.9550
298.15	0.8496	0.8629	0.8773	0.8912	0.9070	0.9273
313.15	0.8337	0.8482	0.8618	0.8754	0.8910	0.9098

estimated precision of the viscosity measurements was 0.2%, and that for density was 0.02%. The mean standard deviation of the efflux time was ±0.1 s, and the maximum and minimum average values of the efflux time were 105.1 s (acetonitrile solution at 313.15 K) and 263.0 s (*N*,*N*-dimethylformamide solution at 253.15 K), respectively. The density measurements were reproducible to within ±2 × 10^{-4} g·cm^{-3} with the pycnometers having a volume of approximately 2 cm^3. At least three flow time and density measurements were performed for each composition and temperature, and the results were averaged.

Results and Discussion

Studying quasibinary mixtures has enabled us to reveal the effect of varying the solvent−solvent ratio on the geometry of excess volume and viscosity properties, which

Table 2. Experimental kinematic viscosities (ν) of solutions containing 0.5 mol·L^{-1} LiClO$_4$, 2.76 × 10^{-2} mol·L^{-1} NaI, 5.51 × 10^{-3} mol·L^{-1} I$_2$ (concentration at 298.15 K)

Acetonitrile (1) + *N*,*N*-Dimethylformamide (2)

	$\nu/(\times 10^6\ \mathrm{m^2 \cdot s^{-1}})$					
T/K	$x_1 = 1$	$x_1 = 0.8586$	$x_1 = 0.6772$	$x_1 = 0.4753$	$x_1 = 0.1715$	$x_1 = 0$
253.15	0.9524	1.1085	1.3468	1.6696	2.2979	2.7322
263.15	0.8368	0.9606	1.1535	1.4065	1.8922	2.219
273.15	0.7422	0.8411	0.9992	1.1999	1.5804	1.8298
298.15	0.5697	0.6275	0.7278	0.845	1.0622	1.1957
313.15	0.496	0.5383	0.6166	0.7034	0.8628	0.957

Acetonitrile (1) + Ethyl Acetate (2)

	$\nu/(\times 10^6\ \mathrm{m^2 \cdot s^{-1}})$					
T/K	$x_1 = 1$	$x_1 = 0.8771$	$x_1 = 0.7259$	$x_1 = 0.5298$	$x_1 = 0.2817$	$x_1 = 0$
253.15	0.9524	1.055	1.118	1.2098	1.284	1.2849
263.15	0.8368	0.9123	0.9636	1.0336	1.0905	1.0894
273.15	0.7422	0.7974	0.8396	0.8932	0.9373	0.9349
298.15	0.5697	0.5924	0.6196	0.6473	0.6711	0.6671
313.15	0.496	0.5071	0.5285	0.5469	0.5634	0.5591

Ethyl acetate (1) + *N*,*N*-Dimethylformamide (2)

	$\nu/(\times 10^6\ \mathrm{m^2 \cdot s^{-1}})$					
T/K	$x_1 = 1$	$x_1 = 0.7295$	$x_1 = 0.5468$	$x_1 = 0.3453$	$x_1 = 0.1579$	$x_1 = 0$
253.15	1.2849	1.901	2.0542	2.2698	2.4956	2.7322
263.15	1.0894	1.5614	1.6925	1.8638	2.0397	2.219
273.15	0.9349	1.3011	1.4145	1.5527	1.692	1.8298
298.15	0.6671	0.87	0.9519	1.0377	1.1201	1.1957
313.15	0.5591	0.7048	0.7737	0.8404	0.9026	0.957

Methyl Ethyl Ketone (1) + Acetonitrile (2)

	$\nu/(\times 10^6\ \mathrm{m^2 \cdot s^{-1}})$						
T/K	$x_1 = 1$	$x_1 = 0.8024$	$x_1 = 0.6620$	$x_1 = 0.5177$	$x_1 = 0.2839$	$x_1 = 0.1413$	$x_1 = 0$
253.15	1.1909	1.2005	1.166	1.1649	1.0791	1.0284	0.9524
263.15	1.0235	1.0313	1.0041	1.0047	0.9351	0.8948	0.8368
273.15	0.8895	0.8959	0.8742	0.8759	0.8188	0.7865	0.7422
298.15	0.6526	0.6567	0.644	0.6472	0.6109	0.5918	0.5697
313.15	0.5549	0.5582	0.5488	0.5524	0.5241	0.5099	0.496

Methylethyl ketone (1) + *N*,*N*-Dimethylformamide (2)

	$\nu/(\times 10^6\ \mathrm{m^2 \cdot s^{-1}})$						
T/K	$x_1 = 1$	$x_1 = 0.8471$	$x_1 = 0.7545$	$x_1 = 0.5504$	$x_1 = 0.3615$	$x_1 = 0.1793$	$x_1 = 0$
253.15	1.1909	1.3888	1.4952	1.7391	2.0283	2.3429	2.7322
263.15	1.0235	1.1823	1.2669	1.4604	1.6851	1.9241	2.219
273.15	0.8895	1.0185	1.0866	1.2421	1.4192	1.6031	1.8298
298.15	0.6526	0.7329	0.7743	0.8689	0.9714	1.0716	1.1957
313.15	0.5549	0.617	0.6485	0.7208	0.7966	0.868	0.957

Methylethyl ketone (1) + Ethyl acetate (2)

	$\nu/(\times 10^6\ \mathrm{m^2 \cdot s^{-1}})$						
T/K	$x_1 = 1$	$x_1 = 0.8696$	$x_1 = 0.8050$	$x_1 = 0.6004$	$x_1 = 0.4197$	$x_1 = 0.2160$	$x_1 = 0$
253.15	1.1909	1.215	1.2205	1.2287	1.2547	1.2708	1.2849
263.15	1.0235	1.0427	1.052	1.0519	1.071	1.0814	1.0894
273.15	0.8895	0.9049	0.9167	0.9108	0.9248	0.9311	0.9349
298.15	0.6526	0.6618	0.6765	0.6629	0.669	0.6694	0.6671
313.15	0.5549	0.5619	0.5771	0.5614	0.5647	0.5632	0.5591

reflect the chemical interactions in the systems (Fialkov, 1992). It seems preferable to analyze the temperature dependences of properties (and their modifications) on the molar fraction of any component. By "component" we will mean an electrolyte solution based on an individual solvent, that is, solvent + LiClO$_4$ + NaI + I$_2$, whose molecular weight was defined as

$$M = \sum_n M_n \cdot y_n \tag{8}$$

where M_n is the molecular weight and y_n is the mole fraction of the n-th constituent part of the solution.

For the temperature dependence of the viscosity, behavior of the Arrhenius type is observed. The activation energies for the viscous flow can be obtained from the following equation:

$$\ln \eta = \ln A\eta + \frac{E_\eta}{R \cdot T} \tag{9}$$

Kinematic viscosity is more preferable for this correlation (Zhytomirskij, 1980).

The viscosity of binary systems formed by molecules of close size and without strong solvent−solvent interactions (Fialkov et al., 1977; Fialkov, 1992) is well-described by

Table 3. Smoothing Coefficients $F_{a,b}$ for Calculations of Pseudomolar Volumes V_{mol}/(cm^3·mol^{-1}) for Eq 13 and Standard Deviations Calculated from Eq 14

	$F_{a,b}$					
a	$b = 0$	$b = 1$	$b = 2$	$b = 3$	$b = 4$	σ/(cm^3·mol^{-1})
			AN + DMFA			
0	55.14	-15.12	-10.49	3.677		0.014
1	6.932×10^{-2}	-2.992×10^{-2}	3.776×10^{-2}	-1.337×10^{-2}		
			AN + EA			
0	62.30	-26.89	-6.893	4.687		0.014
1	0.108	-5.500×10^{-2}	1.941×10^{-2}	-8.812×10^{-3}		
			EA + DMFA			
0	5.514×10	7.838	-0.182	-0.514		0.017
1	6.935×10^{-2}	3.16×10^{-2}	4.744×10^{-2}	2.554×10^{-3}		
			MEK + AN			
0	3.317×10	2.38×10	9.807	-9.666		0.027
1	6.388×10^{-2}	3.732×10^{-2}	-3.691×10^{-2}	3.606×10^{-2}		
			MEK + DMFA			
0	55.14	1.996	12.21	-12.24		0.026
1	6.931×10^{-2}	2.656×10^{-2}	-3.566×10^{-2}	4.015×10^{-2}		
			MEK + EA			
0	62.30	-1.434	-34.27	68.70	-38.31	0.042
1	0.108	-3.435×10^{-2}	0.190	-0.364	0.201	

Table 4. Smoothing Coefficients $F_{a,b}$ for Calculations of the Natural Logarithm of the Kinematic Viscosity ln ν/(ln(m^2·s^{-1})) for Eq 13 and Standard Deviations Calculated from Eq 14

a	$b = 0$	$b = 1$	$b = 2$	$b = 3$	σ
			AN + DMFA		
0	-1.829×10^{1}	1.275	-8.021×10^{-1}	5.335×10^{-1}	2.8×10^{-3}
-1	1.387×10^{3}	-5.756×10^{2}	1.782×10^{2}	-1.243×10^{2}	
			AN + EA		
0	-1.791×10^{1}	4.197×10^{-1}	-8.980×10^{-1}	1.088	5.6×10^{-3}
-1	1.101×10^{3}	-9.040×10^{1}	1.550×10^{2}	-2.934×10^{2}	
			EA + DMFA		
0	-1.831×10^{1}	1.525	-4.512	3.373	0.011
-1	1.393×10^{3}	-6.166×10^{2}	1.522×10^{3}	-1.195×10^{3}	
			MEK + AN		
0	-1.728×10^{1}	-1.204	1.594	-7.427×10^{-1}	7.1×10^{-3}
-1	8.654×10^{2}	4.491×10^{2}	-5.120×10^{2}	2.089×10^{2}	
			MEK + DMFA		
0	-1.829×10^{1}	1.010	-5.901×10^{-1}	2.397×10^{-1}	4.1×10^{-3}
-1	1.388×10^{3}	-4.961×10^{2}	2.564×10^{2}	-1.372×10^{2}	
			MEK + EA		
0	-1.791×10	1.109×10^{-1}	9.898×10^{-1}	-8.172×10^{-1}	6.9×10^{-3}
-1	1.100×10^{3}	-4.569×10	-2.438×10^{2}	1.989×10^{2}	

Table 5. Molar Volume of the Solvents and Solutions Made with Them at 298.15 K

	AN	DMFA	MEK	EA	ref
V_{solvent}/(cm^3·mol^{-1})	52.90	77.40	90.18	98.85	Krestov et al., 1988; Fialkov. 1990
V_{solution}/(cm^3·mol^{-1})	52.21	75.82	86.92	94.48	this work
$V_{\mathrm{solvent}}/V_{\mathrm{solution}}$	1.01	1.02	1.04	1.05	
$100[(\lvert V_{\mathrm{solvent}} - V_{\mathrm{solution}})\rvert/V_{\mathrm{solvent}}]$	1.30	2.04	3.61	4.42	

Table 6. Kinematic Viscosity of the Solvents and Solutions Made with Them at 298.15 K

	AN	MEK	EA	DMFA	ref
ν_{solvent}/(10^7·m^2·s^{-1})	4.39	4.68	4.76	8.43	(Krestov et al.. 1988). (Fialkov. 1990)
ν_{solution}/(10^7·m^2·s^{-1})	5.69	6.54	6.69	11.97	this work
$\nu_{\mathrm{solvent}}/\nu_{\mathrm{solution}}$	1.01	1.02	1.04	1.05	
$100[(\lvert \nu_{\mathrm{solvent}} - \nu_{\mathrm{solution}})\rvert/\nu_{\mathrm{solvent}}]$	29.57	39.73	40.51	41.79	

the equation

$$\eta_{\mathrm{mix}} = {\eta_1}^{x} \cdot {\eta_2}^{1-x} \qquad (10)$$

The deviation of the properties from additivity is

$$\Delta Y = Y - (x \cdot Y_1 + (1 - x) \cdot Y_2) \qquad (11)$$

where Y pseudomolar volume or logarithm of kinematic viscosity of solutions.

The analysis of property deviations has allowed to describe the dependence of a property on composition by a polynom:

$$Y_j = \sum_{0}^{b} C_b \cdot {x_j}^{b} \qquad (12)$$

where the coefficients C_b depend on the temperature as well as researched property data.

Table 7. Values of Extremum Deviation of log of Molar Viscosity for Electrolyte Solutions and Extreme Free Mixing Energy for Binary Solvents

N	solvent	$\Delta\ln(\nu\cdot M)/(\ln(m^2\cdot g\cdot s^{-1}\cdot mol^{-1}))$	$\Delta G_{mix}/(kJ\cdot mol^{-1})$	ref
1	AN−DMFA	−0.610	−0.24	Katime et al., 1984
2	AN−EA	−0.580	−0.28	Sugi and Katayama, 1978
3	MEK−AN	−0.22	0	Van Ness and Kochar, 1967
4	MEK−DMFA	0.084	0.13	Quitzsch et al., 1966
5	EA−DMFA	0.740	0.37	Katime et al., 1984
6	MEK−EA	−0.042		data are lacking

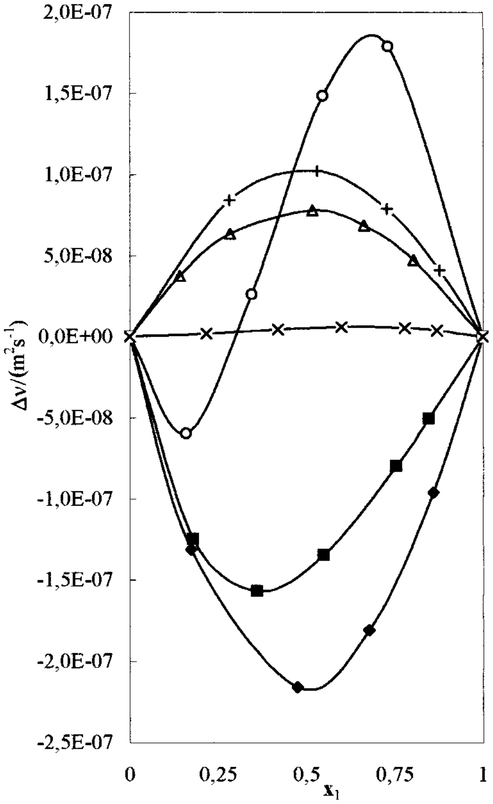

Figure 1. Kinematic viscosity deviation $\Delta\nu$ for electrolyte solutions, based on AN (1) + DMFA (2) (◆), AN (1) + EA (2) (+), EA (1) + DMFA (2) (○), MEK (1) + AN (2) (△), MEK (1) + DMFA (2) (■), MEK (1) + EA (2) (×) at 253.15 K as a function of mole fraction x_1.

In the general case, the dependence of a researched property of a binary system on the temperature and composition leads to a general matrix equation

$$Y_{i,j} = \sum_{b} x_j^{\,b} \cdot \sum_{|a|} F_{|a|,b} \cdot T_i^{\,a} \qquad (13)$$

where $Y_{i,j}$ is the molar additive property (or modification) of the solution at the i-th temperature and the j-th composition, x_j is the molar fraction of a component of the quasibinary system $x = 0...1$, T_i is the temperature (K), b is the maximum order of a power dependence of a property on composition, $b = 0...b$, a is the maximum order of the power dependence of a property on temperature, $a = 0...\pm a$, k is the sequential number of the current composition, $k = 0...k$, and F are the elements of an $(a \times b)$ matrix, which are the coefficients of the temperature dependence of C_b in eq 12.

Therefore, our analysis of the temperature dependences of property deviations ΔY makes it possible to determine the orders of the equations and to describe all the sets of experimental data by a general matrix equation. Having reassigned the values of the smoothing coefficients $F_{a,b}$ in the zeroth $F_{a,0} = 0$, and first, $F_{a,1} =$

$$[-\sum_{2}^{b} F_{a,b}],$$

description of excess properties in the polyterm too.

The standard deviations σ were calculated from the equation

$$\sigma = \left[\frac{\sum (Y_{esp} - Y_{cal})^2}{N - n}\right]^{1/2} \qquad (14)$$

where N is the number of experimental values and n is the number of coefficients used in the correlation, $n = (a \times b)$.

The densities, molar masses, and kinematic viscosities for all six electrolyte systems are presented in Tables 1 and 2, respectively. The values of the smoothing coefficients $F_{a,b}$ and the standard deviations σ are presented in Table 3 for the molar volumes and in Table 4 for the logarithm of the kinematic viscosities. In this work the order of the component−viscosity dependence b varied from 2 to 4, in agreement with the conclusions of Fialkov (1995).

Have compared values of molar volumes for pure solvents and solutions prepared with them (Table 5), we established that the ratio V_{solv}/V_{solut} increases in the series AN−DMFA−MEK−EA according to magnification of the molar volume of a solvent. Relative compressibility is more sensible property. A solution possesing greater molar volume has greater compressibility. This concerns the binary systems in equal measure.

The values of the kinematic viscosity ratio (ν_{solut}/ν_{solv}) increase in the series AN−MEK−EA−DMFA (Table 6) according to magnification of the kinematic viscosity of a solvent. This applies to all binary solvents, as well. The viscosities of electrolyte solutions are higher than those of binary solvents in all cases. The values of the viscosity deviation for binary solvents (Krestov et al., 1988; Kuznetsova et al., 1994) surpass those for electrolyte solutions made with those solvents. The diminution of excess properties (deviations) for molar volumes and for viscosity is bound up with the stabilizing influence of alkali metal cations (Li^+, Na^+) on the structure of solutions (Kuznetsova et al., 1994). The deviations from linear of kinematic viscosity $\Delta\nu$ at 253.15 K are presented in Figure 1. Comparing values of extreme deviation of a log molar viscosity $\Delta\ln(M\cdot n)$ for electrolyte solutions (data of this work) with values of maximum free mixing energy ΔG_{mix} for binary solvents (literature data in Table 7), one can see that a correlaton exists between these data (Figure 2) (number of points in Figure 2 corresponds to ordinal number of binary systems in Table 7). This fact well agrees with transition state theory (Krestov, 1989). Consequently, interaction of components of a binary solvent is a basic contribution in viscosity deviations.

Therefore, the form of eq 13 is applicable to the description of other properties or their deviations of binary (quasibinary) systems with a due correction for the corre-

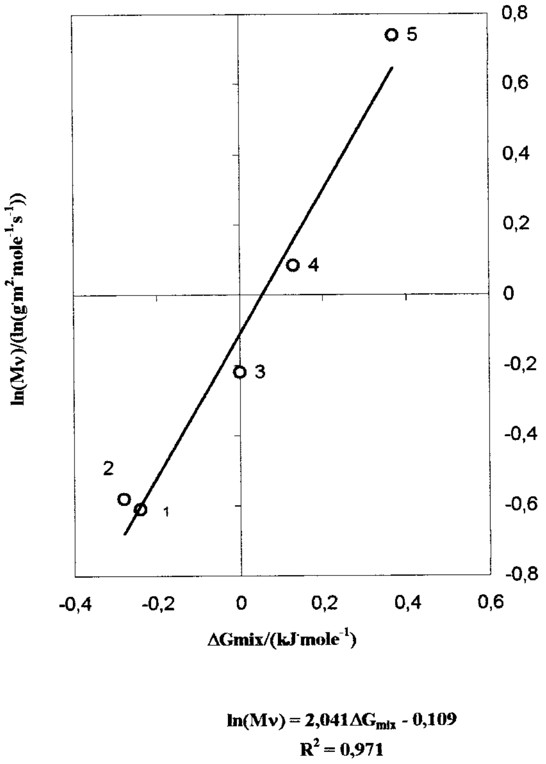

Figure 2. Correlation dependence of the extreme deviation of log molar viscosity versus the extreme free mixing energy of solvents at 298.15 K.

sponding dependence of the considered property (or its modification) on temperature and composition. The representation of experimental results in such a form allows an experiment to be optimized, the properties of binary systems to be forecast at pregiven temperatures and compositions, and the optimal composition of electrolyte to be selected.

Acknowledgment

We thank Dr. Shmakov Sergei L. for his help.

Literature Cited

Fialkov, Ju. Ja. *Solvent as the means of control over the chemical process*; Khimia: Leningrad, 1990.

Fialkov, Ju. Ja. Phycical–chemical analysis of liquid systems and solutions; Naukova dumka: Kiev, 1992.

Fialkov, Ju. Ja. The thermodynamic information about chemical equilibriums found from concentration polythermal dependence of viscosity of liquid systems. *Ukr. Khim. Zh.* **1995,** *61*, 19–23 (in Ukrainian).

Fialkov, Ju. Ja.; Kvitka, A. A.; Zhytomirskij, A. N. Substatiation of mole-additive function of viscosity for binary liquid systems. *Dokl. Akad. Nauk Ukr. SSR*, Ser. B, **1977**, *10*, 923–925.

Gordon, A. J.; Ford, R. A. *The chemists companion*; Wiley-Interscience: New York, 1972.

Handbook of Chemistry, 2nd ed.; Nikolsky, B. P., Ed.; Goskhimizdat: Moscow and Leningrad, 1962; Vol. I, pp 546–993.

Karapetian, Ju. A.; Eychis, V. N. *Physical–chemical properties of electrolyte nonaqueous solutions*; Khimia: Moscow, 1989.

Katime, I.; Cestoros, L. C.; Strazielle, C. Light scattering from binary mixtures of 1,2-dichloroethane, acetonitrile, dimethylformamide and ethyl acetat. Excess Gibbs functions. *J. Chem. Soc., Faraday Trans.* **1984**, *80*, 1215–1224.

Krestov, G. A. *The nonelectrolyte solutions in liquids*; Nauka: Moscow, 1989.

Krestov, G. A.; Afanasyev, V. N.; Efremova, L. S. *Physical–chemical properties of binary solutions*; Khimia: Leningrad, 1988.

Kuznetsova, L. M.; Ovchinnikova E. A.; Avdeyev, V. P.; Mentov, E. V. Influence of temperature, nature and composition of solvent on some physical-chemical properties of solutions lithium perchlorate+acetonitrile+ethyl acetate. *Russ. J. Inorg. Chem.* **1994**, *30* (10), 1338–1340 (in Russian).

Quitzsch, K.; Hoffmann, H. P.; Pfestorf, R.; Geiseler, G. Thermodynamic study of binary liquid mixtures containing formamide homologues. IV Isotermal vapour-phase equilibrium in binary systems with N-disubstituted formamides and strong polar liquids. *J. Prakt. Chem.* **1966**, *34*, 145–152.

Sugi, H.; Katayama, T. Ternary liquid–liquid and miscible binary vapor–liquid equilibrium data for the two systems n-hexan-ethanol-acetonitrile and water-acetonitrile-ethyl acetate. *J. Chem. Eng. Jpn.* **1978**, *11*, 167–172.

Van Ness, H. C.; Kochar, N. K. Vapor–liquid equilibria: acetone–acetonitrile. *J. Chem. Eng. Data* **1967**, *12*, 38–39.

Zhytomirskij, A. N. The temperature dependence of viscositiy of liquids in the transition state theory. *Zh. Fiz. Khim.* **1980**, *54*, 1674–1676 (in Russian).

Received for review November 2, 1998. Accepted June 28, 1999. The author are grateful to the George Soros foundation for major financial support.

JE980271D