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Excess Viscosity η^E, Excess Volume V^E, and Excess Free Energy of Activation ΔG^{*E} at 283, 293, 303, 313, and 323 K for Mixtures of Acetonitrile and Alkyl Benzoates

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Kinematic viscosities were measured for the mixtures (I) acetonitrile + methyl benzoate, (II) acetonitrile + ethyl benzoate, (III) acetonitrile + *n*-propyl benzoate, and (IV) acetonitrile + *n*-butyl benzoate at different temperatures over the entire composition range. From the experimental data, the negative excess viscosities, negative excess free energies of activation, and positive excess molar volumes obtained suggest very interesting intermolecular interactions. The behavior of the mixtures is discussed.

Introduction

Excess thermodynamic functions have been used as a qualitative and quantitative guide to predict the extent of complex formation in binary liquid mixtures of nonelectrolytes (*1*-*4*). The binary liquid mixtures (I) acetonitrile + methyl benzoate, (II) acetonitrile + ethyl benzoate, (III) acetonitrile + *n*-propyl benzoate, and (IV) acetonitrile + *n*-butyl benzoate were chosen due to the polar nature of these five species (acetonitrile, μ = 3.4 D, and esters, $\mu \simeq$ 1.9 D).

Table I. Comparison of the Measured Properties of Pure Components with the Literature Values

	measured			literature	
	temp, °C	ρ, g cm^{-3}	η, cP	ρ, g cm^{-3}	η, cP
acetonitrile	10	0.7921	0.452		
	15				0.375[b]
	20	0.7816	0.408	0.7822,[b] 0.7857[a]	
	25			0.7766[b]	
	30	0.7715	0.371	0.77125[b]	0.325[b]
	40	0.7601	0.339		
	50	0.7495	0.309		
methyl benzoate	10	1.0994	2.435		
	15			1.09334[b]	2.298[b]
	20	1.0892	1.879	1.0888[a]	
	30	1.0800	1.522	1.07091[b]	1.673[b]
	40	1.0680	1.237		
	50	1.0591	1.016		
ethyl benzoate	10	1.0574	2.597		
	15			1.05112[b]	2.407[b]
	20	1.0483	2.013	1.0468[a]	
	30	1.0384	1.597	1.03718[b]	1.751[b]
	40	1.0278	1.284		
	50	1.0200	1.058		
propyl benzoate	10	1.0346	3.451		
	15			1.0274[b]	
	20	1.0262	2.586	1.0232,[b] 1.0230[a]	
	30	1.0187	2.013		
	40	1.0069	1.604		
	41.5			1.0046[b]	
	50	0.9988	1.301		
butyl benzoate	10	1.0147	3.802		
	20	1.0054	2.835	1.000[a]	
	30	0.9972	2.189		
	40	0.9884	1.729		
	50	0.9813	1.387		

[a] Reference *5*. [b] Reference *6*.

Table II. Kinematic Viscosities Measured at Different Temperatures for Mixtures I, II, III, and IV

x_1	283 K	293 K	303 K	313 K	323 K
			Mixture I		
0.000	0.570	0.522	0.481	0.446	0.412
0.134	0.596	0.546	0.499	0.462	0.422
0.255	0.611	0.558	0.510	0.466	0.428
0.373	0.651	0.586	0.531	0.479	0.435
0.480	0.762	0.685	0.612	0.561	0.507
0.570	0.794	0.708	0.629	0.558	0.505
0.666	0.942	0.820	0.716	0.633	0.559
0.752	1.105	0.946	0.810	0.705	0.612
0.837	1.303	1.084	0.921	0.794	0.683
0.922	1.736	1.418	1.163	0.973	0.825
1.000	2.215	1.725	1.410	1.159	0.959
			Mixture II		
0.129	0.628	0.575	0.522	0.480	0.437
0.250	0.648	0.593	0.538	0.495	0.450
0.362	0.718	0.638	0.576	0.523	0.473
0.469	0.786	0.701	0.623	0.563	0.505
0.571	0.892	0.778	0.684	0.613	0.547
0.657	1.039	0.892	0.772	0.684	0.602
0.756	1.296	1.088	0.932	0.803	0.699
0.832	1.608	1.351	1.121	0.949	0.815
0.914	2.120	1.709	1.386	1.146	0.967
1.000	2.456	1.921	1.538	1.250	1.037
			Mixture III		
0.127	0.597	0.544	0.498	0.460	0.421
0.247	0.634	0.579	0.524	0.476	0.434
0.362	0.718	0.640	0.576	0.519	0.471
0.467	0.790	0.698	0.622	0.559	0.500
0.567	0.968	0.835	0.729	0.644	0.570
0.658	1.111	0.946	0.815	0.717	0.626
0.748	1.384	1.159	0.977	0.837	0.720
0.842	1.823	1.561	1.280	1.073	0.901
0.928	2.672	2.058	1.632	1.338	1.111
1.000	3.335	2.520	1.976	1.593	1.303
			Mixture IV		
0.125	0.603	0.555	0.506	0.465	0.406
0.244	0.653	0.589	0.533	0.487	0.443
0.355	0.700	0.628	0.563	0.512	0.467
0.463	0.828	0.723	0.641	0.569	0.512
0.563	0.991	0.853	0.742	0.650	0.533
0.654	1.222	1.036	0.855	0.770	0.673
0.750	1.514	1.249	1.053	0.897	0.732
0.830	2.008	1.629	1.330	1.117	0.960
0.919	2.792	2.164	1.729	1.414	1.166
1.000	3.747	2.820	2.195	1.750	1.414

In the present work densities (ρ) and viscosities (η) of the four mixtures were measured over the entire mole fraction range at 283, 293, 303, 313, and 323 K; these permitted the obtention of the corresponding kinematic viscosities ($\nu = \eta/\rho$). From the experimental results the following thermodynamic functions were calculated: V^E (excess molar volume), η^E (excess viscosity), and ΔG^{*E} (excess molar free energy of activation of flow).

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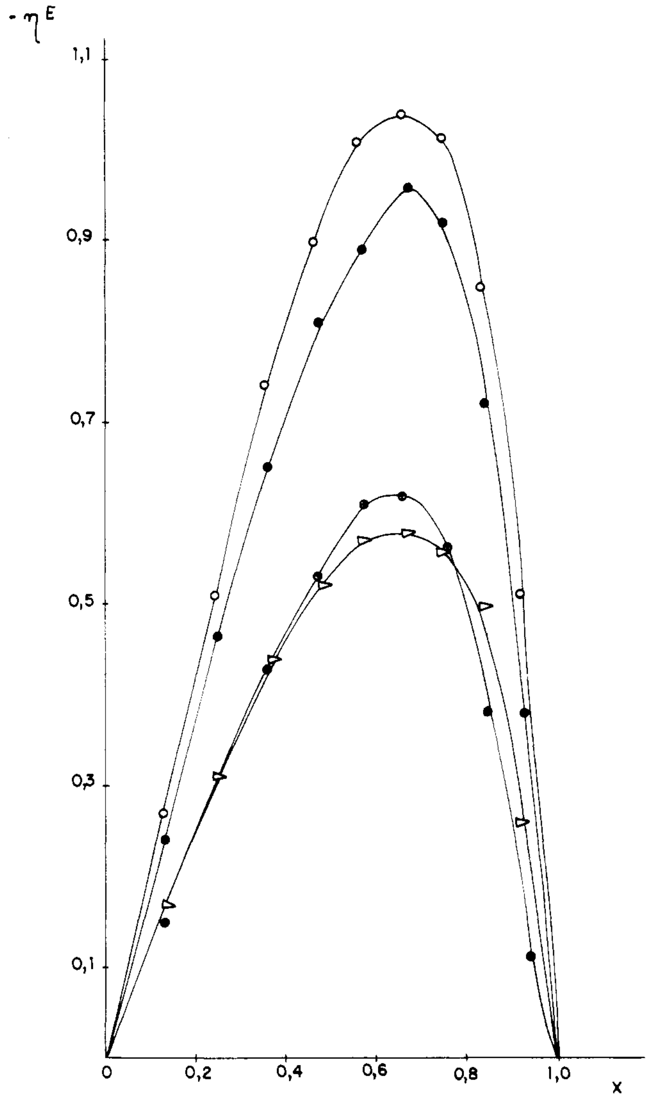

Figure 1. Excess viscosity (cP) variation with ester concentration at 293 K for mixtures I (△), II (⊗), III (●), and IV (○).

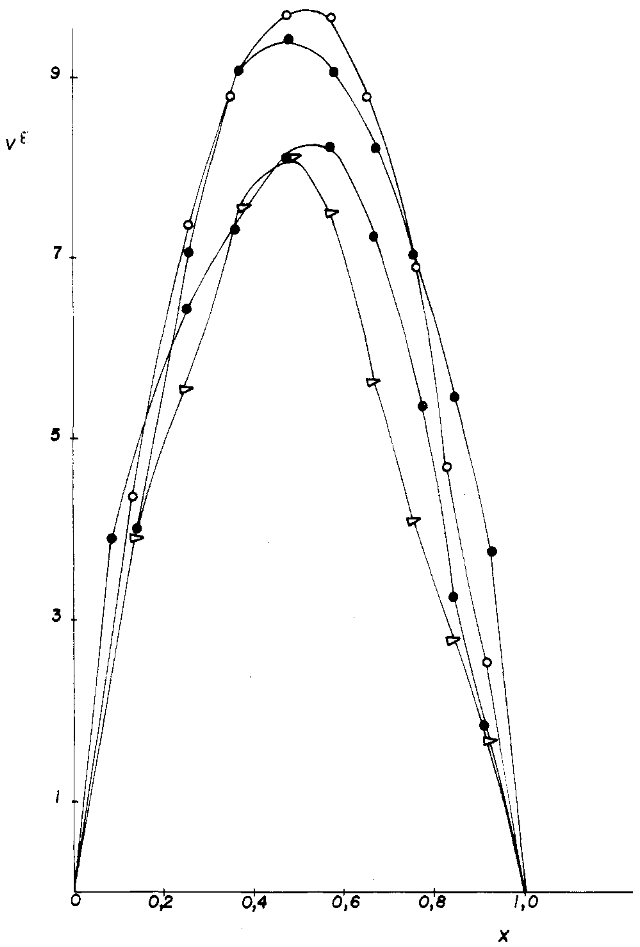

Figure 2. Excess volume (cm^3 mol^{-1}) variation with ester concentration at 293 K for mixtures I (△), II (⊗), III (●), and IV (○).

Experimental Section

Densities were measured with a double levelling pycnometer; it was calibrated at the five working temperatures with quantities weighed within ±0.0001 g. Viscosities were measured with an Ostwald viscometer calibrated with distilled water at different temperatures, with the density and viscosity values taken from the literature (*5*); timings were made within ±0.01 s; two readings were taken at each mole fraction and the mean viscosity did not exceed ±0.004 cP. It was possible to maintain the temperature constant to within ±0.05 K with a P-Selecta thermostat, with the viscometer kept in vertical position throughout.

***Reactants*.** Acetonitrile Panreac p.a. Grade with a stated purity of 99.5 mol % minimum, methyl benzoate (purum >98% GC), and ethyl benzoate (purum >99% GC) were obtained from Fluka. These were purified by suitable procedures involving distillation and drying (*6*); *n*-propyl and *n*-butyl benzoates were synthesized by a Fisher esterification (*7*); water was continuously eliminated by means of a Dean-Stark trap and the reflux time was reduced from 10 h to 5; the ester obtained was washed with water and extracted with ether; anhydrous Na_2SO_4 was used for drying and $NaHCO_3$ to eliminate the excess benzoic acid; the purification was carried out in a vacuum line within a range of 122–124 °C for *n*-propyl benzoate and 156–158 °C for *n*-butyl benzoate.

Characterization of the esters was carried out with a NMR-H1 spectrometer R-24B, 60 MHz Hitachi-Perkin Elmer; purity was assessed with a Perkin Elmer 990 gas chromatograph; with a Hewlett Packard 3390A integrator for a column in liquid phase over a solid Supelcoport 100/120, $1^1/_8$ in., the working temperatures being 250, 275, and 150 °C for the detector, injector, and oven, respectively; the carrier gas was nitrogen at 20 cm^3 min^{-1} and the combustion gases were air and hydrogen at 240 and 30 cm^3 min^{-1}, respectively. The purity obtained was 99.95% GC for the two esters. Mixtures were prepared by mixing weighed amounts of the pure liquids and care was taken to prevent evaporation. Properties of the pure components appear in Table I.

Results

The excess thermodynamic functions (*8*) were calculated with the following equations

$$\eta^E = \eta - (X_1\eta_1 + X_2\eta_2) \tag{1}$$

$$V^E = V - (X_1V_1 + X_2V_2) \tag{2}$$

$$\Delta G^{*E} = RT(\ln \eta V - (X_1 \ln \eta_1V_1 + X_2 \ln \eta_2V_2)) \tag{3}$$

where η, η_1, and η_2 are the viscosities of the mixture and of the pure components and V, V_1, and V_2 are the molar volumes

Table III. Excess Viscosities (cP), Excess Volumes ($cm^3\ mol^{-1}$), and Excess Free Energy ($kJ\ mol^{-1}$) for Mixtures I–IV

		283 K			293 K			303 K			313 K			323 K		
mixture	x_1	$-\eta^E$	V^E	$-\Delta G^{*E}$	$-\eta^E$	V^E	$-\Delta G^{*E}$	$-\eta^E$	V^E	$-\Delta G^{*E}$	$-\eta^E$	V^E	$-\Delta G^{*E}$	$-\eta^E$	V^E	$-\Delta G^{*E}$
I	0.134	0.22	3.84	2.62	0.16	3.95	0.65	0.12	4.06	−0.15	0.09	4.07	−0.82	0.07	4.25	−0.48
	0.255	0.43	5.49	11.48	0.30	5.50	7.56	0.23	5.70	5.99	0.18	5.85	5.45	0.13	6.03	2.28
	0.373	0.61	7.53	18.96	0.44	7.57	15.54	0.34	7.91	13.28	0.26	8.03	13.61	0.20	8.27	13.99
	0.480	0.73	8.02	23.13	0.52	8.13	18.29	0.40	8.28	16.44	0.30	8.37	13.80	0.22	8.62	10.63
	0.570	0.81	7.53	25.90	0.57	7.64	21.07	0.43	7.63	19.07	0.32	7.79	17.14	0.24	7.92	14.17
	0.666	0.83	5.57	27.56	0.58	5.61	21.98	0.44	5.82	19.38	0.33	5.76	18.64	0.24	5.92	15.10
	0.752	0.81	4.08	24.41	0.55	4.08	19.92	0.42	4.09	18.70	0.31	4.02	17.10	0.23	4.25	14.34
	0.837	0.74	2.70	22.80	0.51	2.78	19.66	0.38	2.71	18.35	0.28	2.60	16.37	0.20	2.74	14.36
	0.922	0.41	1.73	9.71	0.25	1.69	6.60	0.20	1.74	7.38	0.15	1.59	6.95	0.10	1.69	5.33
II	0.129	0.21	3.80	−3.43	0.15	3.90	−5.53	0.11	4.03	−6.05	0.08	4.11	−7.13	0.06	4.15	−7.39
	0.250	0.43	6.27	4.95	0.31	6.44	1.30	0.23	6.73	−0.63	0.17	6.85	−3.80	0.13	7.11	−4.60
	0.362	0.59	7.09	9.08	0.43	7.32	6.71	0.32	7.49	3.74	0.23	7.62	1.10	0.18	7.78	0.99
	0.469	0.74	7.96	15.75	0.53	8.11	11.54	0.39	8.35	8.84	0.29	8.57	5.38	0.22	8.71	3.21
	0.571	0.84	7.99	19.57	0.61	8.27	16.28	0.45	8.46	13.36	0.32	8.87	9.46	0.25	8.97	6.85
	0.657	0.87	7.26	19.75	0.62	7.24	16.29	0.45	7.46	13.85	0.33	7.72	9.79	0.25	8.00	7.70
	0.756	0.80	5.20	15.69	0.56	5.35	13.05	0.40	5.36	10.01	0.29	5.53	7.46	0.21	5.96	5.34
	0.832	0.59	3.15	8.75	0.38	3.26	4.55	0.27	3.25	3.44	0.18	3.15	1.57	0.13	3.35	−0.14
	0.914	0.20	0.88	−2.46	0.11	0.98	−4.28	0.07	0.87	−4.45	0.04	0.76	−5.28	0.02	0.87	−6.24
III	0.127	0.34	3.88	31.25	0.24	3.96	1.35	0.18	4.05	−0.05	0.13	4.13	−1.51	0.10	4.38	−2.33
	0.247	0.66	6.85	11.49	0.46	7.06	7.45	0.34	7.28	5.36	0.26	7.25	4.11	0.20	7.69	2.29
	0.362	0.91	8.83	17.05	0.65	9.16	13.43	0.48	9.47	10.32	0.36	9.58	8.25	0.28	10.05	5.61
	0.467	1.15	9.23	26.28	0.81	9.38	21.77	0.59	9.88	18.22	0.45	10.06	15.16	0.34	10.30	12.73
	0.567	1.26	8.59	25.74	0.88	9.04	21.70	0.64	9.16	18.48	0.48	9.40	15.94	0.37	9.59	13.41
	0.658	1.38	7.86	30.79	0.96	8.23	26.48	0.70	8.62	23.43	0.52	8.55	19.94	0.39	8.69	18.06
	0.748	1.35	6.46	28.57	0.92	7.05	23.40	0.67	7.16	21.64	0.49	7.15	19.71	0.38	7.28	17.91
	0.842	1.18	5.01	22.53	0.72	5.43	13.82	0.51	5.69	12.27	0.37	5.57	10.93	0.29	5.74	10.43
	0.928	0.54	3.49	4.87	0.38	3.80	−4.53	0.28	4.12	4.72	0.20	3.84	4.16	0.15	3.93	3.57
IV	0.125	0.38	4.33	1.26	0.26	4.38	−1.55	0.19	4.45	−2.74	0.14	4.55	−3.77	0.10	4.78	−0.03
	0.244	0.72	7.15	8.33	0.51	7.34	5.37	0.38	7.59	3.11	0.28	7.57	1.22	0.22	8.13	1.01
	0.355	1.04	8.62	19.71	0.73	8.82	15.47	0.54	9.13	12.69	0.40	9.42	9.40	0.31	9.80	5.80
	0.463	1.27	9.40	23.64	0.90	9.65	20.10	0.66	10.27	16.67	0.50	10.30	14.47	0.38	10.71	11.02
	0.563	1.44	9.41	26.76	1.01	9.64	22.90	0.73	9.94	19.82	0.55	10.29	18.71	0.41	10.60	17.44
	0.654	1.52	8.57	27.42	1.05	8.75	24.09	0.75	9.03	21.03	0.55	9.25	19.28	0.45	9.47	21.89
	0.750	1.50	6.75	26.26	1.03	6.91	22.09	0.75	7.13	19.28	0.55	7.39	16.07	0.37	7.62	13.03
	0.830	1.27	4.60	18.88	0.85	4.68	15.34	0.61	4.83	13.90	0.43	4.99	11.59	0.30	5.16	7.59
	0.919	0.75	2.51	8.48	0.50	2.51	7.40	0.35	2.59	6.38	0.24	2.71	5.14	0.18	2.82	4.25

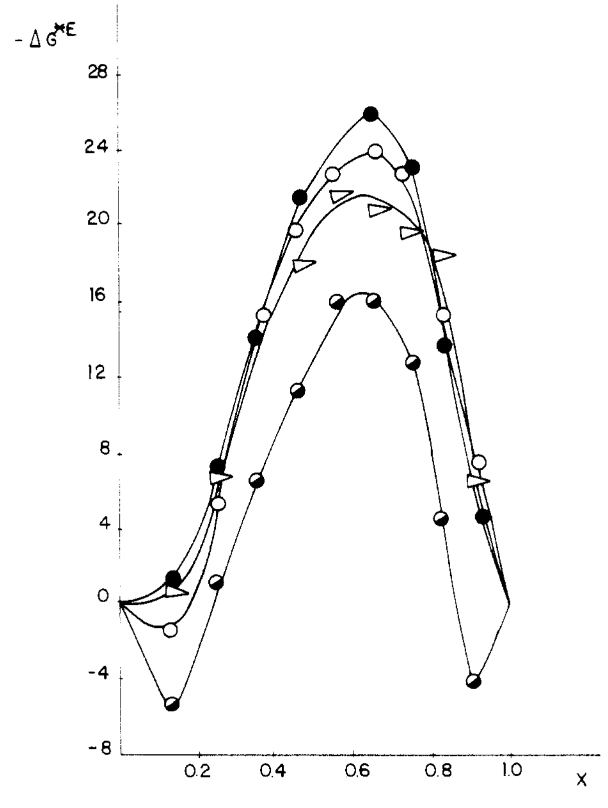

Figure 3. Excess free energy of activation ($kJ\ mol^{-1}$) variation with ester concentration at 293 K for mixtures I (△), II (⊗), III (●), and IV (○).

of the mixture and of the pure components. The molar volume V of the mixture is defined as

$$V = (X_1M_1 + X_2M_2)/\rho \qquad (4)$$

where M_1 and M_2 are the molecular weights of the components, ρ is the density of the mixture, and X_i is the mole fraction of the component i in solution.

Table II contains the kinematic viscosities measured at five different temperatures for mixtures I–IV. The excess thermodynamic function values are shown in Table III for each of the four mixtures studied; these values were fitted at each temperature to a polynomial function by the method of unweighted least squares:

$$Y^E = X_1X_2 \sum_{i=0}^{n-1} a_i(X_1 - X_2)^i \qquad (5)$$

The n coefficients a_i, multilinear correlation coefficients R, and standard deviations $S(Y)$, calculated according to eq 6, are shown in Tables IV, V, and VI.

$$S(Y) = \left[\frac{\sum(Y^E{}_{\text{exptl}} - Y^E{}_{\text{calcd}})^2}{n_{\text{exptl}} - n}\right]^{1/2} \qquad (6)$$

In nonelectrolyte systems, positive deviations from ideal behavior are attributed to dispersion forces (*9*) and negative deviations to geometric considerations (*10*). Attempts have been made to explain the direction and magnitude of the excess viscosity and excess volume behavior of the liquid mixtures.

Table III shows that excess viscosities are negative in the entire range of temperatures and mole fraction, with a minimum

Table IV. Least-Squares Coefficients of Results by Eq 5 for Excess Viscosities

mixture	T, K	a_0	a_1	a_2	a_3	a_4	a_5	R	$S(Y)$
I	283	-3.00	-1.34	-1.38	-5.15	-0.10	5.70	0.998	0.154
	293	-2.13	-0.61	-0.88	-5.45	0.12	6.75	0.996	0.154
	303	-1.63	-0.49	-0.50	-3.62	-0.28	4.24	0.998	0.114
	313	-1.24	-0.34	-0.37	-2.46	-0.04	2.75	0.998	0.098
	323	-0.94	-0.21	-0.23	-2.06	-0.12	2.36	0.999	0.071
II	283	-3.08	-1.90	-2.32	-2.46	5.11	6.75	0.998	0.129
	293	-2.22	-1.48	-1.52	-0.43	4.11	3.58	0.999	0.089
	303	-1.64	-1.08	-0.99	-0.03	2.94	2.33	0.999	0.066
	313	-1.21	-0.75	-0.67	-0.06	2.24	1.90	0.999	0.066
	323	-0.95	-0.55	0.09	-0.80	0.79	2.93	0.999	0.063
III	283	-4.70	-2.33	-3.72	-9.88	2.60	12.97	0.998	0.208
	293	-3.35	-2.30	-1.73	-0.50	1.36	1.05	0.999	0.109
	303	-2.48	-1.87	-0.91	1.78	0.26	-2.65	0.998	0.133
	313	-1.85	-1.21	-0.87	0.22	0.79	0.20	0.999	0.095
	323	-1.42	-0.87	-0.71	-0.07	0.65	0.18	0.999	0.079
IV	283	-5.36	-3.32	-2.81	-4.10	1.18	4.76	0.999	0.147
	293	-3.79	-2.35	-1.61	-1.51	0.71	1.54	0.999	0.159
	303	-2.77	-1.59	-1.09	-1.41	0.58	1.62	0.999	0.126
	313	-2.07	-1.10	-0.75	-1.15	0.51	1.45	0.998	0.125
	323	-1.62	-0.90	-0.22	0.70	-0.34	-1.08	0.997	0.108

Table V. Least-Squares Coefficients of Results by Eq 5 for Excess Volumes

mixture	T, K	a_0	a_1	a_2	a_3	a_4	a_5	a_6	R	$S(Y)$
I	283	32.43	-9.34	-45.08	12.88	64.87	-21.00		0.998	0.547
	293	32.86	-10.22	-47.83	21.54	70.40	-35.88		0.998	0.478
	303	33.35	-12.59	-38.60	31.00	23.13	-48.89	54.07	0.998	0.229
	313	34.04	-11.82	-48.02	16.05	66.19	-25.76		0.998	0.514
	323	34.65	-14.23	-39.88	34.03	27.07	-52.51	48.59	0.999	0.399
II	283	33.03	6.45	-12.50	-60.73	49.91	54.57	-85.39	0.999	0.373
	293	32.21	7.37	-9.75	-62.23	37.77	53.79	-73.91	0.999	0.282
	303	33.99	7.49	-16.68	-74.57	73.23	72.57	-117.98	0.999	0.139
	313	35.10	10.09	-16.59	-86.93	64.29	82.49	-109.88	0.999	0.464
	323	35.59	10.89	-12.86	-94.84	64.45	96.32	-120.08	0.999	0.149
III	283	36.33	-8.52	5.97	26.36	-56.69	-7.30	91.70	0.999	0.409
	293	37.31	-7.58	16.31	30.74	-89.23	-12.34	122.98	0.999	0.227
	303	38.76	-8.74	14.23	34.22	-88.58	-11.06	130.25	0.999	0.685
	313	39.64	-9.56	5.04	40.15	-63.76	-23.87	107.87	0.999	0.255
	323	40.59	-12.42	8.78	46.37	-68.87	-27.76	109.64	0.999	0.284
IV	283	37.83	3.14	5.01	-32.01	-42.11	31.11	47.63	0.998	0.300
	293	38.80	4.32	1.39	-40.41	-24.32	41.98	25.24	0.995	0.508
	303	39.99	3.15	5.37	-35.46	-42.16	37.83	41.66	0.997	0.389
	313	41.44	1.81	3.55	-17.83	-54.95	13.04	68.25	0.993	0.558
	323	40.84	1.42	3.39	-29.85	-36.44	32.85	41.61	0.998	0.401

Table VI. Least-Squares Coefficients of Results by Eq 5 for Excess Molar Free Energy of Activation

mixture	T, K	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	R	$S(Y)$
I	283	-95.10	-140.31	95.56	700.65	858.88	-3039.57	-815.25	3320.59	0.999	4.644
	293	-74.85	-87.82	-142.51	702.70	1016.13	-3612.72	-1429.50	4210.48	0.999	2.636
	303	-67.07	-73.72	-84.47	450.95	595.38	-2454.00	-841.28	663.79	0.999	2.121
	313	-59.04	-67.32	-218.82	584.96	1347.92	-3226.53	-1772.43	3808.99	0.997	8.104
	323	-15.48	5.82	-34.89	-3.35	80.79	-120.62	-193.09	118.36	0.999	0.142
II	283	-69.70	-96.57	126.31	155.90	-523.04	37.91	947.49	-255.85	0.999	0.037
	293	-51.92	-88.78	-17.47	101.40	285.98				0.999	1.795
	303	-40.67	-86.52	-2.84	100.92	240.83				0.999	2.673
	313	-26.90	-72.30	18.74	14.06	189.79	112.76			0.999	1.569
	323	-17.07	-72.22	7.36	50.54	202.84	69.58			0.999	1.092
III	283	-99.24	-52.34	-91.38	-330.00	202.25	523.10			0.992	5.719
	293	-92.34	-106.31	33.81	91.75	63.14				0.998	3.598
	303	-78.24	-121.59	14.27	200.12	88.07	-154.89			0.997	5.640
	313	-65.39	-90.79	7.41	49.58	86.48				0.993	7.021
	323	-54.39	-94.81	-7.66	55.52	100.88				0.995	5.904
IV	283	-98.55	-53.35	-186.25	-294.46	1026.07	463.32	-1051.66		0.999	0.517
	293	-81.80	-36.94	-128.11	-313.88	821.95	427.52	-847.30		0.998	0.987
	303	-72.09	-74.14	8.46	-13.93	102.51				0.992	4.749
	313	-65.06	-93.40	-89.42	-14.69	699.57	100.54	-695.79		0.999	0.591
	323	-54.48	-72.47	-72.47	149.28	163.13				0.998	4.155

well-defined; according to Fort and Moore (*11*), excess viscosities are negative in systems of unequal molecular size in which dispersion forces are dominant. Figure 1 shows the variation of excess viscosities with ester mole fraction at 20 °C; the behavior observed is similar at all temperatures studied: excess viscosities become more negative with increasing length of the lateral chain of the ester and lead to a minimum near $X_1 \simeq 0.66$; this minimum points to the existence of intermolecular interactions with complex formation (*12*). The four curves are not regularly spaced and a marked gap is observed in excess viscosities from mixture II to III.

In the systems studied, excess volumes are positive throughout the whole range of mole fractions and lead to maxima showing little variation with temperature. Figure 2 shows the results obtained for the four mixtures at 20 °C; with increasing chain length the maximum increases and is located near $X_1 \simeq 0.5$; positive V^E values have been explained in terms of complex formation (*13*). However, Palmer and Smith (*14*), based on their investigation on 1-propanol + dichloromethane mixtures at 25 °C, attributed positive V^E to a breaking of hydrogen bridges, caused by dichloromethane. The formation of high-volume complexes would justify the high values obtained for excess volumes.

According to Reed (*15*) and Meyer (16), excess free energy of activation may be considered a reliable measure to detect the presence of interactions between molecules; positive values of ΔG^{*E} can be seen in binary mixtures where specific interactions between molecules take place; negative ΔG^{*E} indicate a characteristic behavior of mixtures in which dispersion forces are dominant (*17*). In this investigation high negative values of ΔG^{*E} were obtained for mixtures I–IV; in some cases positive ΔG^{*E} values appeared in the proximity of pure components. These results are shown in Figure 3, with a minimum located at $X_1 \simeq 0.66$.

Glossary

μ	dipole moment, D
η	viscosity, cP
ν	kinematic viscosity, m^2 s^{-1}
ρ	density, g cm^{-3}
η^E	excess viscosity, cP
V^E	excess volume, cm^3 mol^{-1}
ΔG^{*E}	excess free energy, kJ mol^{-1}
X_1	ester mole fraction
X_2	acetonitrile mole fraction
Y^E	thermodynamic excess property
a_i	polynomial coefficients
n_{exptl}	number of data points
n	number of adjustable parameters
T	temperature, K
V	molar volume, cm^3 mol^{-1}
R	gas constant
M	molecular weight

Registry No. Acetonitrile, 75-05-8; methyl benzoate, 93-58-3; ethyl benzoate, 93-89-0; propyl benzoate, 2315-68-6; butyl benzoate, 136-60-7.

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Partial Molar Volumes and Compressibilities of 1–1 Type Chlorides, Bromides, $[Ph_4P]Cl$, and $Na[Ph_4B]$ in Water–Acetone Mixtures

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The densities and adiabatic compressibilities have been measured at 298.15 K for solutions of NaCl, KCl, CsCl, NaBr, KBr, $[Ph_4P]Cl$, and $Na[Ph_4B]$ dissolved in water–acetone mixtures up to acetone content 50 wt %. The partial molar volume V_2^0 and partial molar adiabatic compressibilities K_s^0 have been calculated. Variation with composition of the solvent system was more remarkable for K_s^0 than for V_2^0. In solvents containing more than 10 wt % of acetone, K_s^0 of $[Ph_4P]Cl$ and $Na[Ph_4B]$ were positive, while all the other 1–1 type salts always had negative K_s^0 values. Ionic division of K_s^0 of an electrolyte based on the assumption $K_s^0([Ph_4P]^+) = K_s^0([Ph_4B]^-)$ seems unacceptable in this mixed solvent.

Introduction

It is well-known that the partial molar volume and partial molar adiabatic compressibility are very helpful parameters for elucidation of various aspects of solute–solvent interactions. Information deduced from the respective parameters is complementary to each other. Behavior of electrolytes in mixed solvents, especially in those containing water as one of the components, is currently arousing considerable interest because of its importance as fundamental data in solution chemistry and potentiality in industrial purposes. However, in addition to the paucity of physical constants of binary mixed solvents in general, the thermodynamic behavior of an electrolyte dissolved in such mixed solvents often shows highly complex solvent composition dependence. Therefore, for discussion of the solute–