J. Chem. Eng. Data 1991, 36, 269-274

Shear Viscosities of Binary Liquid Mixtures: 2-Pyrrolidone with 1-Alkanols[†]

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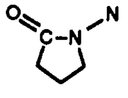
Excess viscosities, excess volumes, and free energies of activation for viscous flow of the binary mixtures 2-pyrrolidone + methanol, + ethanol, + 1-propanol, + 1-butanol, and + 1-pentanol were calculated at five different temperatures from density and viscosity measurements. The results obtained suggest that the breaking of the self-associations existing in the pure liquids is partly balanced by the heteroassociations formed among the molecules of the binary mixtures. These heteroassociations decrease with decreasing temperature and increasing chain length of the alcohol. The small excess volumes calculated denote weak interactions, in accordance with the different shape and size of the mixing molecules.

Introduction

2-Pyrrolidone is a cyclic amide (lactam) to which the basic structural peptide bond -NH-CO- confers theoretically interesting properties as solvent; 2-pyrrolidone adopts cis conformation and, in addition to the acid -C═O and basic -NH groups, exhibits the property of self-association, serving as a model for the hydrogen bonding of bases in nucleic acids. On the basis of ab initio studies, an "enveloped" conformation is assigned to 2-pyrrolidone,



with an angle of about 27° that can be easily inverted at 30-40 K (*1*). Experiments carried out in highly dilute solutions, to determine the structure of 2-pyrrolidone, prove association by intermolecular hydrogen bonding, limited to dimerization (*2*, *3*). At high concentrations, IR, Raman, and dielectric polarization measurements, performed in nonpolar solvents, indicate the existence of dimers, trimers, and higher oligomers (*4*-*6*).

Studies have also been made on self-association of vapor 1-alkanols, showing the existence of monomers, dimers, and tetramers (*7*). Self-associations of 1-alkanols in nonpolar solvents have also been investigated extensively, the intermolecular interactions being justified through hydrogen bondings (*8*, *9*).

Only a few references were found on the binary liquid mixtures 2-pyrrolidone + 1-alkanols. Pirilä-Honkanen and Ruostesuo (*10*) reported excess volumes of mixtures 2-pyrrolidone-2-propanol, and Dachwitz et al. (*11*) made measurements of dielectric relaxation of mixtures 2-pyrrolidone and derivatives with alcohol and water, reporting 1:1 association with methanol. Similar conclusions were drawn by Beine et al. (*12*). Excess volumes of water-2-pyrrolidone mixtures at 25 °C were calculated by David (*13*). Nevertheless, more abundant information is available on the amide-alcohol systems: *N*,*N*-dimethylacetamide, *N*-methylacetamide, and *N*,*N*-dimethylaniline with aliphatic alcohols (*14a*-*c*), *N*-methylacetamide and *N*,*N*-dimethylacetamide with 2,2,2-trifluoroethanol (*14d*) and 2-phenylethanol (*14e*), as well as *N*,*N*-diethylmethanesulfonamide with aliphatic alcohols (*14f*).

In this paper, values of excess volumes, excess viscosities, and excess free energies of activation for flow are reported on binary liquid mixtures 2-pyrrolidone + methanol, + ethanol, + 1-propanol, + 1-butanol, and + 1-pentanol at five different temperatures; the intermolecular interactions existing in these mixtures are analyzed as functions of temperature and of the chain length of the alcohol.

Experimental Section

Reactants. The pure liquids were commercially available from Merck. 2-Pyrrolidone and 1-pentanol were purified by vacuum distillation over CaO and the other alcohols by simple distillation over CaH_2. The purity was assessed by GC and the density, and viscosity values measured were compared with those found in the literature (Table I).

General Procedure. Densities were measured with a double-capillary pycnometer; it was calibrated at the five working temperatures with quantities weighted within ±0.0001 g. Viscosities were measured with a Cannon-Fenske viscometer calibrated with distilled water at different temperatures, with the density and viscosity values taken from the literature (*20*). The temperature was kept constant within ±0.01 °C with a thermostat, heater, and refrigerator. Densities and viscosities were reproducible to ±0.0001 g cm^{-3} and ±0.004 cP, respectively. Mixtures were prepared by weight in volumetric flasks of appropriate volume according to the expected error in each component; a design to prevent evaporation was introduced into the flasks. The pure liquids were dried with molecular sieve type 4A of Serva.

Results and Discussion

Considering the mixing of two pure liquids as a thermodynamic process, the excess functions may be defined as the balance between the final state, with the two components forming the solution, and the initial state, corresponding to pure components. Thus, excess viscosities, excess volumes, and free energies of activation are calculated according to following equations:

$$\eta^E = \eta - (X_1\eta_1 + X_2\eta_2) \quad (1)$$

$$V^E = V - (X_1V_1 + X_2V_2) \quad (2)$$

$$G^{*E} = RT[\ln \nu\bar{M} - (X_1 \ln \nu_1M_1 + X_2 \ln \nu_2M_2)] \quad (3)$$

where η, η_1, and η_2 are the absolute viscosities (cP) of the mixture and of the pure components, ν, ν_1, and ν_2 ($m^2\ s^{-1}$) the corresponding kinematic viscosities (calculated as the quotient between η and ρ (g cm^{-3})), and V, V_1, and V_2 the molar volumes of the mixture and of the pure components; V is defined as

$$V = \bar{M}/\rho = (X_1M_1 + X_2M_2)/\rho \quad (4)$$

where M_1 and M_2 are the molar masses, ρ is the density of the

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[†] Paper presented at the 4th International Conference on Thermodynamics of Solutions of Non-Electrolytes, Santiago de Compostela, Spain, 24-29 Sept 1989.

0021-9568/91/1736-0269$02.50/0

Table I. Comparison of Measured Densities (ρ, g cm^{-3}) and Viscosities (η, cP) of Pure Components with Literature Value

	2-pyrrolidone		methanol		ethanol		1-propanol		1-butanol		1-pentanol	
temp, °C	lit.	exptl	lit.	exptl	lit.	exptl	lit.	exptl	lit.	exptl	lit.	exptl
(A) Densities												
25	1.107[a]	1.1080	0.76664[a]	0.7687	0.78504[a]	0.7850	0.79975[a]	0.7995	0.8095[b]	0.8059	0.8115[a]	0.8109
30		1.1034	0.7816[c]	0.7818	0.7807[c]	0.7807	0.7955[c]	0.7956	0.8018[c]	0.8019	0.8074[c]	0.8072
40		1.0950		0.7723		0.7721		0.7873		0.7941		0.7997
50	1.087[a]	1.0869		0.7632		0.7632		0.7789		0.7862		0.7920
60		1.087			0.75438[d]	0.7543	0.77064[d]	0.7706	0.77822[d]	0.7782		0.7844
(B) Viscosities												
25	13.033[a]	13.0927	0.547[b]	0.5415		1.0600		1.8994		2.0397	3.347[a]	3.3952
30		10.6983	0.516[b]	0.5063	1.003	0.9627	1.720[b]	1.6825	2.300[b]	2.2266		2.9404
40		7.4041	0.456[b]	0.4434	0.834[b]	0.7968	1.405[b]	1.3242	1.782[b]	1.7201		2.2243
50		5.3718	0.403[b]	0.3895	0.702[b]	0.6632	1.130[b]	1.0514	1.411[b]	1.3434		1.7033
60		4.0633			0.592[b]	0.5562		0.8454		1.0643		1.3296

[a] Reference 20. [b] Reference 21. [c] Reference 22. [d] Reference 14f.

Table II. Negative Excess Viscosities ($-\eta^E$, cP) of Binary Mixtures at Different Temperatures for the Five Binary Mixtures

		$-\eta^E$				
mixture	X_1	298 K	303 K	313 K	323 K	333 K
2-pyrrolidone–methanol	0.0998	1.060	0.843	0.550	0.375	
	0.1977	2.035	1.612	1.045	0.711	
	0.2964	2.924	2.307	1.488	1.004	
	0.3979	3.701	2.909	1.855	1.243	
	0.4942	4.271	3.337	2.107	1.397	
	0.5944	4.602	3.563	2.215	1.465	
	0.6912	4.576	3.546	2.182	1.412	
	0.7887	4.083	3.120	1.887	1.206	
	0.8968	2.654	2.001	1.186	0.743	
2-pyrrolidone–ethanol	0.0986	1.042	0.828	0.542	0.370	0.265
	0.1993	1.024	1.605	1.043	0.710	0.506
	0.3034	2.935	2.317	1.494	1.012	0.718
	0.3960	3.628	2.853	1.826	1.228	0.866
	0.4924	4.204	3.289	2.080	1.394	0.977
	0.5941	4.588	3.570	2.239	1.477	1.024
	0.6919	4.620	3.573	2.210	1.443	0.996
	0.7963	4.101	3.133	1.908	1.226	0.830
	0.8933	2.842	2.146	1.271	0.809	0.543
2-pyrrolidone–1-propanol	0.996	1.066	0.845	0.546	0.374	0.263
	0.1989	1.991	1.577	1.020	0.693	0.491
	0.2999	2.805	2.198	1.419	0.964	0.682
	0.3971	3.473	2.729	1.745	1.171	0.824
	0.4980	4.000	3.127	1.982	1.320	0.925
	0.6003	4.299	3.341	2.094	1.385	0.957
	0.6987	4.253	3.282	2.034	1.332	0.902
	0.8000	3.772	2.885	1.762	1.141	0.780
	0.8907	2.682	2.033	1.222	0.781	0.531
2-pyrrolidone–1-butanol	0.1017	1.140	0.915	0.589	0.398	0.279
	0.1992	2.069	1.640	1.062	0.716	0.503
	0.3030	2.909	2.297	1.476	0.995	0.699
	0.3989	3.545	2.790	1.784	1.196	0.838
	0.4919	4.001	3.130	1.972	1.303	0.896
	0.5900	4.334	3.378	2.124	1.403	0.975
	0.6941	4.354	3.368	2.094	1.371	0.945
	0.7945	3.914	3.002	1.822	1.188	0.810
	0.8986	2.650	2.014	1.210	0.759	0.516
2-pyrrolidone–1-pentanol	0.1175	1.354	1.073	0.691	0.465	0.319
	0.2056	2.156	1.704	1.099	0.734	0.512
	0.3026	2.888	2.280	1.463	0.980	0.684
	0.3975	3.474	2.730	1.743	1.165	0.813
	0.4934	3.926	3.075	1.952	1.300	0.906
	0.5914	4.195	3.270	2.059	1.363	0.949
	0.6925	4.196	3.240	2.023	1.331	0.920
	0.8010	3.734	2.872	1.765	1.150	0.791
	0.9248	2.092	1.590	0.956	0.617	0.418

Table III. Negative Excess Volumes ($-V^E$, cm^3 mol^{-1}) of Binary Mixtures at Different Temperatures for the Five Binary Mixtures

		$-V^E$				
mixture	X_1	298 K	303 K	313 K	323 K	333 K
2-pyrrolidone–methanol	0.0998	0.393	0.403	0.440	0.463	
	0.1977	0.588	0.606	0.665	0.710	
	0.2964	0.685	0.713	0.785	0.843	
	0.3979	0.697	0.724	0.809	0.858	
	0.4942	0.657	0.690	0.767	0.809	
	0.5944	0.571	0.596	0.650	0.673	
	0.6912	0.459	0.485	0.526	0.534	
	0.7887	0.315	0.346	0.374	0.380	
	0.8968	0.139	0.178	0.189	0.196	
2-pyrrolidone–ethanol	0.0986	0.256	0.260	0.292	0.321	0.385
	0.1993	0.430	0.438	0.488	0.519	0.596
	0.3034	0.500	0.515	0.578	0.635	0.742
	0.3960	0.532	0.557	0.620	0.676	0.742
	0.4924	0.508	0.534	0.582	0.611	0.664
	0.5941	0.453	0.488	0.528	0.619	0.693
	0.6919	0.369	0.404	0.426	0.449	0.492
	0.7963	0.263	0.292	0.619	0.336	0.394
	0.8933	0.127	0.159	0.177	0.191	0.224
2-pyrrolidone–1-propanol	0.0996	0.157	0.158	0.168	0.161	0.175
	0.1989	0.251	0.253	0.267	0.287	0.313
	0.2999	0.313	0.317	0.346	0.362	0.394
	0.3971	0.326	0.348	0.372	0.398	0.445
	0.4980	0.323	0.342	0.378	0.398	0.461
	0.6003	0.300	0.327	0.359	0.391	0.435
	0.6987	0.278	0.307	0.336	0.354	0.409
	0.8000	0.187	0.217	0.243	0.252	0.300
	0.8907	0.100	0.136	0.153	0.162	0.196
2-pyrrolidone–1-butanol	0.1017	0.078	0.079	0.100	0.101	0.113
	0.1992	0.143	0.147	0.167	0.179	0.224
	0.3030	0.182	0.192	0.215	0.222	0.267
	0.3989	0.209	0.218	0.244	0.267	0.307
	0.4919	0.230	0.242	0.273	0.300	0.338
	0.5900	0.219	0.238	0.264	0.298	0.355
	0.6941	0.187	0.212	0.245	0.261	0.309
	0.7945	0.131	0.164	0.200	0.249	0.329
	0.8986	0.075	0.095	0.103	0.125	0.157
2-pyrrolidone–1-pentanol	0.1175	0.041	0.044	0.038	0.049	0.064
	0.2056	0.081	0.087	0.082	0.098	0.112
	0.3026	0.111	0.111	0.121	0.130	0.153
	0.3975	0.126	0.138	0.161	0.174	0.213
	0.4934	0.139	0.158	0.197	0.203	0.249
	0.5914	0.138	0.155	0.172	0.183	0.222
	0.6925	0.125	0.148	0.169	0.192	0.231
	0.8010	0.096	0.115	0.134	0.148	0.177
	0.9248	0.038	0.067	0.081	0.083	0.119

mixture, and X_i is the mole fraction of component i in the mixture.

Tables II–IV contain the excess functions of the five binary mixtures at the five temperatures; the values η^E, V^E, and G^{*E} were fitted at each temperature for each of the five mixtures to a polynomial function by the method of unweighted least-squares

$$Y^E = X_1(1 - X_1)\sum_{n=0}^{4} a_n(2X_1 - 1)^n \qquad (5)$$

Table IV. Negative Free Energy of Activation of Flow ($-G^{*E}$, kJ mol^{-1}) at Different Temperatures for the Five Binary Mixtures

		$-G^{*E}$				
mixture	X_1	298 K	303 K	313 K	323 K	333 K
2-pyrrolidone–methanol	0.0998	0.002	–0.011	–0.035	–0.056	–0.077
	0.1977	0.011	–0.013	–0.057	–0.092	–0.127
	0.2964	0.019	–0.017	–0.070	–0.120	–0.165
	0.3979	0.025	–0.013	–0.085	–0.142	–0.191
	0.4942	0.041	–0.004	–0.083	–0.147	–0.198
	0.5944	0.049	–0.006	–0.092	–0.138	–0.196
	0.6912	0.053	0.022	–0.053	–0.117	–0.160
	0.7887	0.060	0.025	–0.037	–0.086	–0.122
	0.8968	0.041	0.020	–0.016	–0.045	–0.066
2-pyrrolidone–ethanol	0.0986	0.300	0.278	0.240	0.202	0.175
	0.1993	0.495	0.459	0.392	0.330	0.284
	0.3034	0.611	0.561	0.474	0.402	0.341
	0.3960	0.658	0.604	0.506	0.422	0.352
	0.4924	0.673	0.612	0.511	0.422	0.350
	0.5941	0.651	0.592	0.486	0.396	0.324
	0.6919	0.579	0.526	0.426	0.345	0.283
	0.7963	0.446	0.398	0.322	0.256	0.203
	0.8933	0.269	0.240	0.187	0.151	0.120
2-pyrrolidone–1-propanol	0.0996	0.418	0.392	0.338	0.301	0.256
	0.1989	0.669	0.630	0.552	0.486	0.425
	0.2999	0.813	0.745	0.661	0.590	0.516
	0.3971	0.885	0.830	0.726	0.633	0.551
	0.4980	0.896	0.837	0.728	0.629	0.549
	0.6003	0.844	0.786	0.679	0.587	0.501
	0.6987	0.731	0.677	0.583	0.502	0.413
	0.8000	0.571	0.527	0.451	0.387	0.335
	0.8907	0.358	0.330	0.281	0.240	0.210
2-pyrrolidone–1-butanol	0.1017	0.478	0.461	0.402	0.354	0.309
	0.1992	0.774	0.731	0.650	0.571	0.501
	0.3030	0.961	0.906	0.799	0.708	0.623
	0.3989	1.041	0.981	0.867	0.764	0.674
	0.4919	1.043	0.978	0.847	0.730	0.619
	0.5900	1.014	0.951	0.834	0.730	0.642
	0.6941	0.897	0.839	0.733	0.640	0.562
	0.7945	0.710	0.661	0.564	0.498	0.436
	0.8986	0.414	0.386	0.332	0.280	0.248
2-pyrrolidone–1-pentanol	0.1175	0.541	0.511	0.452	0.395	0.344
	0.2056	0.787	0.742	0.661	0.580	0.510
	0.3026	0.951	0.898	0.799	0.705	0.621
	0.3975	1.034	0.974	0.865	0.765	0.676
	0.4934	1.057	0.997	0.884	0.782	0.693
	0.5914	1.017	0.957	0.847	0.747	0.666
	0.6925	0.910	0.849	0.751	0.664	0.588
	0.8010	0.715	0.670	0.588	0.519	0.462
	0.9248	0.339	0.318	0.277	0.246	0.219

X_1 being the mole fraction that refers to 2-pyrrolidone. The n coefficients a_n and standard deviations $S(Y)$, calculated according to eq 6, are shown in Tables V–VII, Φ being the

$$S(Y) = \left| \frac{\sum (Y^E_{exptl} - Y^E_{calcd})^2}{\Phi} \right|^{1/2} \qquad (6)$$

number of degrees of freedom. Excess volumes were negative throughout and increased with increasing temperature. Excess viscosities were also negative but decreased with increasing temperature; this behavior was also observed in binary mixtures 2-pyrrolidone + ethanol, + 1-propanol, + 1-butanol, and + 1-pentanol with respect to G^{*E}. In the case of methanol, G^{*E} becomes negative at 298 K within the entire composition range. At 303 K, however, an inflection point appears at $X_1 \sim 0.60$, and, at higher temperatures, a maximum value was obtained at $X_1 \sim 0.50$, G^{*E} being positive at all compositions (Figure 1). According to Reed (*15*), Meyer (*16*), and Oswal (*17*), positive G^{*E} values are observed in binary mixtures where specific interactions (hydrogen bonding, dipole–dipole, etc.) among the mixing molecules are prevalent, whereas negative G^{*E} values denote a characteristic behavior of liquid systems where dispersion forces are prevalent (*18*).

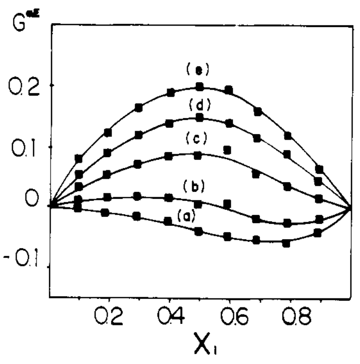

Figure 1. Free energies of activation of flow of the system 2-pyrrolidone–methanol at (a) 298 K, (b) 303 K, (c) 313 K, (d) 323 K, and (e) 333 K.

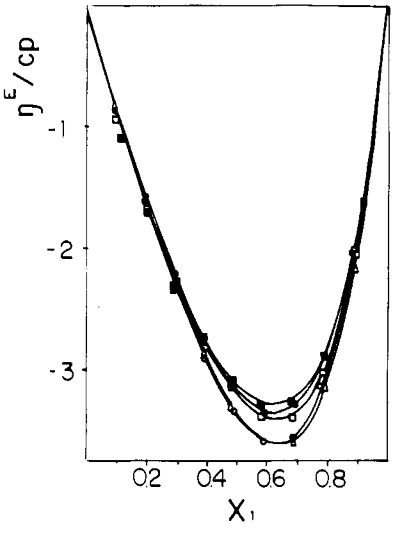

Figure 2. Excess viscosity vs mole fraction at 303 K of the systems 2-pyrrolidone + methanol (○), + ethanol (△), + 1-propanol (●), + 1-butanol (□), and + 1-pentanol (■).

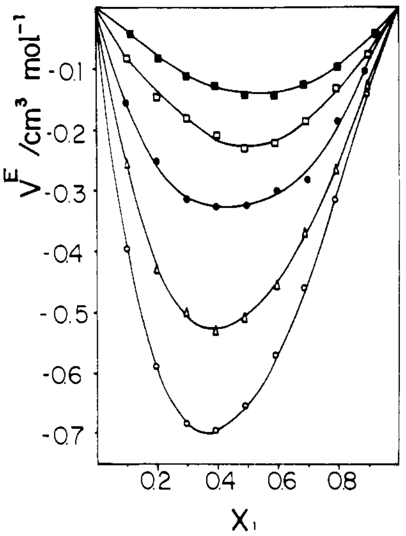

Figure 3. Excess molar volumes vs mole fraction at 298 K of the systems 2-pyrrolidone + methanol (○), + ethanol (△), + 1-propanol (●), + 1-butanol (□), and 1-pentanol (■).

Also interesting is a comparative study of the excess functions of the five systems at the same temperature; at constant temperature, excess viscosities were not affected to a con-

Table V. Least-Squares Coefficients for Excess Viscosities Obtained According to Equation 5

mixture	T, K	a_0	a_1	a_2	a_3	a_4	$S(Y)$
2-pyrrolidone–methanol	298	-17.176	9.196	-4.315	2.266	-0.943	0.005
	303	-13.408	6.843	-3.250	1.383	-0.139	0.007
	313	-8.459	3.805	-1.557	0.671	-0.125	0.007
	323	-5.617	2.261	-0.800	0.258	0.028	0.003
2-pyrrolidone–ethanol	298	-16.977	9.639	-5.382	2.857	-1.267	0.006
	303	-13.282	7.213	-3.884	1.767	-0.636	0.006
	313	-8.418	4.162	-2.108	0.669	-0.023	0.001
	323	-5.613	2.497	-1.133	0.370	-0.045	0.002
	333	-3.929	1.603	-0.676	0.155	0.033	0.003
2-pyrrolidone–1-propanol	298	-16.029	8.165	-4.599	2.974	-2.468	0.008
	303	-12.532	6.114	-3.127	1.917	-2.014	0.009
	313	-7.939	3.483	-1.722	1.027	-0.962	0.004
	323	-5.289	2.106	-1.079	0.575	-0.428	0.002
	333	-3.695	1.254	-0.501	0.598	-0.583	0.006
2-pyrrolidone–1-butanol	298	-16.190	8.110	-6.095	3.555	-1.735	0.009
	303	-12.680	6.051	-4.326	2.377	-1.546	0.009
	313	-8.018	3.474	-2.537	1.179	-0.504	0.014
	323	-5.312	2.166	-1.863	0.520	0.418	0.011
	333	-3.685	1.413	-1.349	0.343	0.527	0.013
2-pyrrolidone–1-pentanol	298	-15.801	7.236	-5.656	3.645	-3.371	0.005
	303	-12.367	5.356	-4.131	2.652	-2.554	0.006
	313	-7.844	3.133	-2.422	1.360	-1.258	0.004
	323	-5.221	1.960	-1.446	0.856	-0.784	0.002
	333	-3.641	1.327	-0.931	0.537	-0.457	0.002

Table VI. Least-Squares Coefficients for Excess Volumes According to Equation 5

mixture	T, K	a_0	a_1	a_2	a_3	a_4	$S(Y)$
2-pyrrolidone–methanol	298	-2.612	-1.303	-0.485	-0.736	-0.049	0.004
	303	-2.733	-1.367	-0.431	-0.337	-0.449	0.005
	313	-3.030	-1.608	-0.241	-0.207	-0.683	0.007
	323	-3.183	-1.952	-0.249	0.163	-0.715	0.007
2-pyrrolidone–ethanol	298	-2.016	-0.797	-0.438	-0.284	0.431	0.007
	303	-2.138	-0.711	-0.341	-0.149	0.125	0.006
	313	-2.334	-0.974	-0.445	0.141	0.088	0.008
	323	-2.571	-0.990	-0.104	-0.046	-0.384	0.031
	333	-2.816	-1.177	-0.811	-0.069	0.066	0.044
2-pyrrolidone–1-propanol	298	-1.293	-0.180	-0.638	-0.435	0.869	0.008
	303	-1.386	-0.091	-0.482	-0.230	0.367	0.009
	313	-1.518	-0.058	-0.454	-0.198	0.293	0.008
	323	-1.618	-0.080	-0.496	-0.097	0.582	0.008
	333	-1.834	-0.010	-0.398	0.011	0.297	0.009
2-pyrrolidone–1-butanol	298	-0.909	0.022	0.301	-0.133	-0.310	0.002
	303	-0.956	0.126	-0.002	-0.070	0.001	0.006
	313	-1.065	0.228	-0.205	-0.293	0.171	0.007
	323	-1.166	0.318	-0.262	-0.155	0.097	0.011
	333	-1.318	0.399	-1.183	-0.022	1.234	0.013
2-pyrrolidone–1-pentanol	298	-0.549	0.081	-0.112	0.056	0.356	0.002
	303	-0.623	0.153	0.120	0.174	-0.304	0.006
	313	-0.727	0.160	0.392	0.438	-0.592	0.006
	323	-0.777	0.225	0.198	0.270	-0.368	0.011
	333	-0.961	0.259	0.653	0.450	-1.329	0.013

siderable degree by the particular alcohol, the same shape and profile being obtained for the five mixtures with a minimum value at $X_1 \sim 0.63$ (Figure 2). According to Fort et al. (*19*), excess viscosities are negative in mixtures of unequal size in which dispersion forces are dominant. On the other hand, these excess volumes are small (Figure 3), revealing that these interactions are not intense, as usually occurs in systems formed by mixing molecules of different geometry. These interactions become smaller at constant temperature, as the chain length of the alcohol increases. Figure 4 shows the behavior of G^{*E} at 328 K for all the binary mixtures: formation of 2-pyrrolidone–methanol heteroassociations can be inferred, the extent of which depends on temperature; the small values of G^{*E} (Figure 1) suggest that dispersion forces, responsible for the breaking of the self-associations existing in the pure liquids (negative G^{*E}), and specific interactions, which produce heteroassociations (negative G^{*E}), are quite balanced. Indeed, the value $G^{*E} = 0$ is reached for $X_1 = 0.57$ at 303 K; the position of the maxima suggests 1:1 heteroassociations, in good agreement with the results reported for the same system from relaxation dielectric measurements (*11*). The values of G^{*E} become still more negative as the chain length of the alcohol increases, suggesting an increase of dispersion forces in that direction; however, the excess volumes indicate that the capabilities of the alcohols to break up the molecular associations decrease with an increase in the chain length, which should not be in agreement with the values of G^{*E} reported, and with the dielectric constants $D = 32.70$ (methanol), $D = 24.55$ (ethanol), $D = 20.33$ (1-propanol), $D = 17.51$ (1-butanol), and $D = 13.90$ (1-pentanol). Thus, it seems clear that the behavior of these binary mixtures may be interpreted only on the basis of the existence of heteroassociations of decreasing intensity with the chain length of the alcohol and decreasing temperature, leading to more negative G^{*E}. The results reported are in agreement

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

mixture	T, K	a_0	a_1	a_2	a_3	a_4	$S(Y)$
2-pyrrolidone–methanol	298	−0.154	0.207	−0.177	0.092	0.066	0.003
	303	0.035	0.184	−0.320	0.055	0.301	0.006
	313	0.359	0.051	−0.387	0.162	0.426	0.008
	323	0.591	0.030	−0.220	0.082	0.259	0.001
	333	0.805	0.012	−0.242	0.131	0.339	0.003
2-pyrrolidone–ethanol	298	−2.695	−0.160	−0.691	−0.316	0.099	0.004
	303	−2.457	−0.189	−0.665	−0.342	0.172	0.008
	313	−2.040	−0.257	−0.560	−0.346	0.170	0.005
	323	−1.686	−0.329	−0.446	−0.181	0.126	0.002
	333	−1.394	−0.342	−0.442	−0.195	0.186	0.008
2-pyrrolidone–1-propanol	298	−3.579	−0.444	−0.576	−0.241	−0.602	0.004
	303	−3.342	−0.405	−0.350	−0.325	−0.857	0.009
	313	−2.906	−0.475	−0.396	−0.121	−0.475	0.005
	323	−2.518	−0.503	−0.508	−0.073	−0.194	0.002
	333	−2.180	−0.622	−0.288	0.324	−0.439	0.008
2-pyrrolidone–1-butanol	298	−4.197	−0.383	−1.279	−0.083	0.318	0.005
	303	−3.945	−0.385	−1.102	−0.189	0.044	0.006
	313	−3.449	−0.419	−1.091	−0.142	−0.344	0.012
	323	−2.999	−0.397	−1.313	−0.154	0.946	0.014
	333	−2.600	−0.365	−1.427	−0.073	1.231	0.022
2-pyrrolidone–1-pentanol	298	−4.220	−0.257	−1.105	−0.120	−0.303	0.001
	303	−3.975	−0.294	−0.960	−0.065	−0.396	0.003
	313	−3.525	−0.297	−0.849	−0.059	−0.273	0.002
	323	−3.117	−0.270	−0.708	0.024	−0.250	0.001
	333	−2.765	−0.212	−0.589	0.047	−0.217	0.029

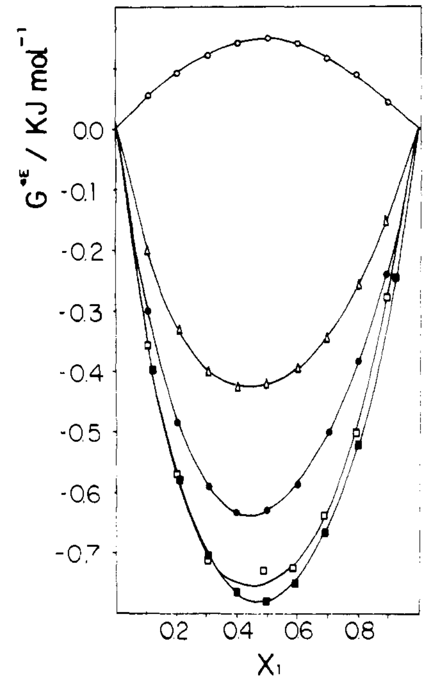

Figure 4. Free energies of activation of flow vs mole fraction at 323 K of the systems 2-pyrrolidone + methanol (○), + ethanol (△), + 1-propanol (●), + 1-butanol (□), and + 1-pentanol (■).

with those of Pikkarainen (*14*) on alcohol–amide mixtures, in which the heteroassociations at 303.15 K are supposed to be of less importance than the breaking of self-associations of alcohols by the hydrogen bonding and dipole–dipole effects existing in the pure components. Pirilä-Honkanen et al. (*10*) justify the excess volumes calculated at 303.15 and 323.15 K for 2-pyrrolidone–2-propanol by the prevalence of the interaction between the carbonyl group of 2-pyrrolidone and the OH group of 2-propanol over the other effects; V^E values were always negative, with absolute values lower and close to those reported in this paper. Recently, Al-Azzawi et al. (*23*) reported negative V^E for binary mixtures of 2-pyrrolidone–water, with minima at $X_1 \sim 0.4$; these V^E were small and were ascribed to hydrogen bond interactions.

The conclusions drawn in this work are in agreement with others reported based on the activation thermodynamic functions calculated for same mixtures (*24*).

Glossary

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}
G^{*E}	free energy of activation for flow, kJ mol^{-1}
X_1	2-pyrrolidone mole fraction
Y^E	thermodynamic excess function
a_n	polynomial coefficients
Φ	degrees of freedom
T	temperature, K
V	molar volume, cm^3 mol^{-1}
R	gas constant
M	molar mass

Registry No. 2-Pyrrolidinone, 616-45-5; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 1-butanol, 71-36-3; 1-pentanol, 71-41-0.

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Received for review April 23, 1990. Accepted January 14, 1991.

Isobaric Vapor–Liquid Equilibrium Data for the Ethanol–Water–Potassium Acetate and Ethanol–Water–(Potassium Acetate/Sodium Acetate) Systems

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Isobaric experimental data of vapor–liquid equilibrium for the ethanol–water–potassium acetate system at different mole fractions of potassium acetate (0.060, 0.080, and 0.100) are presented. Also, the vapor–liquid equilibrium for the ethanol–water–(potassium acetate/sodium acetate) (2:1) system at different mole fractions of salt (0.040 and 0.060) is studied. For each system, both the activity coefficient and relative volatility were calculated. The effect of the salt mixture on the vapor–liquid equilibrium is the same as the effect of potassium acetate being alone.

Introduction

A salt dissolved in a mixture of volatile components may affect the activities of the components through the formation of complexes. If this interaction is selective, the relative volatility of the volatile components may change drastically, depending on the salt concentration, and thus facilitate the separation of close-boiling components or even of azeotropic mixtures. This effect has been used successfully for obtaining absolute ethanol from aqueous solutions.

The industrial success of salt-effect extractive distillation is conditioned to the solid agent recovery. One of the techniques described (*1*) to maintain an anhydrous hygroscopic salt during feeding to the reflux stream is as a molten salt. Then the economy of the process depends strongly on the salt melting point.

Therefore, a good solid agent to rectify the ethanol–water mixtures must be sufficiently soluble in both components, produce an important salting-out effect, and have a relatively low melting point. Potassium acetate seems to be the most effective salt (*2*).

Several authors (*3–9*) have studied the vapor–liquid equilibrium of the ethanol–water system saturated with potassium acetate. Only Schmitt (*10*) has reported vapor–liquid equilibrium data for ethanol and water with varying concentrations of potassium acetate below saturation.

Gorhan (*1*) suggested the use of potassium and sodium acetate mixtures as extractive agents to obtain anhydrous ethanol, but he has not reported vapor–liquid equilibrium data for this system. The synergistic effects attributable to salt mixtures can decrease the melting point of the mixture. We have verified that a potassium and sodium acetate mixture in a molar ratio of 2:1 has a minimum melting point of about 245 °C (the potassium acetate melting point is 292 °C). This fact should make this mixture especially suitable as an extractive agent for rectifying ethanol–water mixtures.

The present study determines the vapor–liquid equilibrium of ethanol–water–potassium acetate and ethanol–water–(potassium acetate/sodium acetate) (2:1) systems to check the efficiency of the latter in relation to the former.

Experimental Section

The chemicals were absolute ethanol (Baker Analyzed Reagent, >99.5 wt %), distilled water, potassium acetate (Probus, 98 wt %), and sodium acetate (Panreac, 98 wt %).

The equilibrium apparatus was a recirculating still of the type described by Walas (*11*) (Labodest model), manufactured by Fischer Labor-und Verfahrenstechnik. The vapor–liquid equilibrium data were obtained at atmospheric pressure, which remained practically constant in the range 764 ± 2 mmHg. The vapor pressure of water with a varying concentration of salt was also measured with the same apparatus.

For each experimental point, the feed to the recirculating still was prepared gravimetrically by using a Sartorius analytical balance with a precision of ±0.0001 g. The fit of the salt molar fraction in the feed with the desired quantity (0.04, 0.06, 0.08, or 0.10) was obtained with a precision of ±0.0005. The same procedure was used for preparing the densimeter calibration (used for the measurement of the liquid-phase composition) and gas chromatograph calibration (used for the measurement of the vapor-phase composition).

Compositions of the condensed vapor phase were analyzed by using a Hewlett-Packard 5700 A gas chromatograph with a thermal conductivity detector, connected to a Hewlett-Packard 3394 A integrator. The chromatographic column (2 m × $^1/_8$ in.) was packed with Porapak P. The gas carrier was Helium flowing at 50 cm^3/min, and the column temperature was 110 °C. The accuracy of the measured vapor-phase mole fraction is ±0.0015.

Water and ethanol compositions in the liquid phase containing dissolved salt were obtained by density measurements with an Anton Paar DMA 55 densimeter matched to a Julabo circulator with proportional temperature control and an automatic drift correction system that kept the samples at 25.00 ± 0.01 °C. The accuracy of the liquid-phase mole fractions depends on the accuracy of the salt mole fractions in the mixture. It was assumed that the salt mole fraction in the liquid phase in equilibrium was the same as that initially fed to the recirculating

0021-9568/91/1736-0274$02.50/0