Viscosity of Binary Mixtures of Propylamine with Alkanols at Moderately High Pressures

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Experimental measurements are reported for the viscosity and the density of the four binary mixtures of propylamine with methanol, ethanol, 1-propanol, and 1-butanol. The systems studied exhibit self-association and strong cross-association due to the strong hydrogen bonding between the hydroxyl and the amine groups. The measurements were conducted at 25 °C and in a pressure range from atmospheric to 520 bar for the viscosity and from atmospheric to 340 bar for the density. A self-centering falling body viscometer has been used for the viscosity measurements and a vibrating tube densitometer for the density measurements. Calculated excess volumes and compressibilities are reported.

Introduction

Numerous processes in the chemical industry are conducted at moderately high pressures, one typical example being supercritical fluid extraction. In these processes, often, the fluid system is a binary or multicomponent mixture. In the case of supercritical extraction, as an example, design of the pumping system of the solvent requires knowledge of the density and viscosity of the modifier at pressures up to 500 bar. Usually the modifier is a highly polar system such as methanol or a mixture of alkanols.

Over the last few years we have been conducting a systematic study of the basic thermophysical properties of representative hydrogen-bonded systems, primarily liquids, such as volumetric properties, phase equilibria, heats of mixing, interfacial properties, and viscosities (*1*–*4*). These properties are correlated with an equation-of-state model of associated solutions (*5*, *6*) hereafter referred to as LFAS (lattice fluid associated solutions) model. Recently (*4*) we described a falling-body viscometer which may be used for the measurement of viscosity at high pressures.

In this work we present new results on densities and viscosities of four alkanol + amine mixtures at moderately high pressures. These results are useful for estimating the limiting quantity of the variation of the viscosity, η, with pressure, P, $(\mathrm{d} \ln \eta/\mathrm{d}P)_T$, as P tends to 0. This limiting quantity is of central importance in equation-of-state theories of viscosity (*7*).

Experimental Section

All materials used were pro-analysis grade from Merck and were used as received. Their purity was verified by gas–liquid chromatography and was better than 99.8% for methanol, 99.5% for ethanol, 1-propanol, and 1-butanol, and 99.0 mol % for propylamine. Pure component properties are shown in Table 1. The mixtures were prepared by mass with a precision of ±0.0001 g. Precautions were taken in order to minimize evaporation losses during storage and preparation of the solutions.

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Table 1. Pure Component Properties at 298.15 K

	ϱ/(kg·m^{-3})		η/(mPa·s)	
liquid	measd	lit.	measd	lit
methanol	786.7	787.0[a]	0.546	0.546[a]
ethanol	785.1	785.2[b]	1.083	1.081[b]
1-propanol	799.6	800.0[b]	1.968	1.942[b]
1-butanol	805.9	806.0[c]	2.578	2.600[d]
propylamine	711.3	711.0[e]	0.365	

[a] Reference 8. [b] Reference 9. [c] Reference 10. [d] Reference 11. [e] Reference 12.

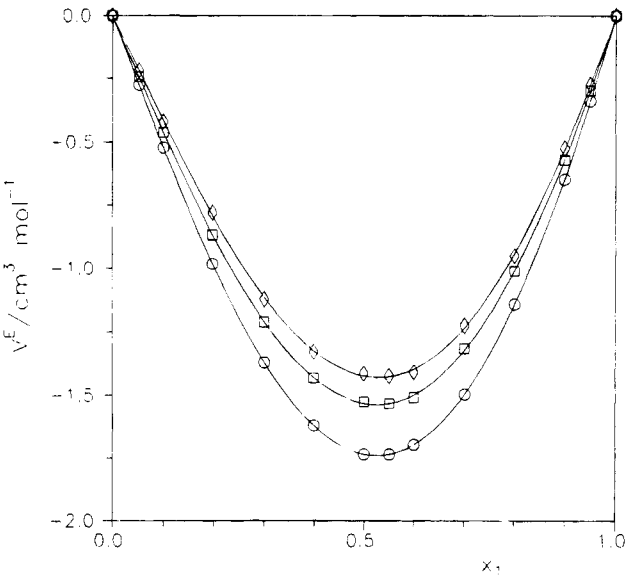

Figure 1. Excess volume for the system methanol (1) + propylamine (2) at 298.15 K: ○, P = 1.01 bar; □, P = 199.5 bar, ◇, P = 339.0 bar; —, eq 2.

The liquid densities, ϱ, were measured with two Anton Paar vibrating tube densitometers, Models 60/602 (atmospheric pressure) and 60/512 (high pressure). The estimated error in the density at atmospheric pressure is ±5 × 10^{-6}g·cm^{-3} while the corresponding error in the density at higher pressures is ±1 × 10^{-4} g·cm^{-3}.

For the measurement of the viscosity, η, at high pressures a self-centering falling body viscometer has been constructed in which a sinker falls axially down the center of a vertical circular tube containing the liquid whose viscosity is to be measured. The viscometer, its operating

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Table 2. Experimental Densities, Excess Volumes, and Compressibilities for the System Methanol (1) + Propylamine (2) at 298.15 K

P/bar	ρ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}	ρ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}	ρ/(g·cm^{-3})	V_E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}
		$x_1 = 0.0000$			$x_1 = 0.0520$			$x_1 = 0.0997$	
1.0	0.7113	0.000	1.173	0.7157	−0.277	1.159	0.7199	−0.522	1.142
20.0	0.7129	0.000	1.152	0.7173	−0.274	1.137	0.7215	−0.516	1.121
59.9	0.7161	0.000	1.110	0.7205	−0.268	1.094	0.7246	−0.504	1.079
79.8	0.7177	0.000	1.090	0.7220	−0.265	1.074	0.7262	−0.498	1.059
119.7	0.7207	0.000	1.053	0.7251	−0.258	1.037	0.7292	−0.486	1.022
159.6	0.7237	0.000	1.020	0.7280	−0.252	1.002	0.7321	−0.474	0.988
199.5	0.7266	0.000	0.989	0.7309	−0.245	0.971	0.7350	−0.462	0.957
239.3	0.7295	0.000	0.961	0.7337	−0.238	0.942	0.7377	−0.451	0.928
289.2	0.7329	0.000	0.930	0.7371	−0.229	0.910	0.7411	−0.436	0.896
339.0	0.7363	0.000	0.903	0.7404	−0.220	0.881	0.7444	−0.421	0.868
		$x_1 = 0.1975$			$x_1 = 0.3001$			$x_1 = 0.3989$	
1.0	0.7290	−0.982	1.113	0.7388	−1.370	1.066	0.7481	−1.619	1.039
20.0	0.7305	−0.971	1.091	0.7403	−1.352	1.047	0.7495	−1.5999	1.021
59.9	0.7336	−0.948	1.047	0.7433	−1.318	1.010	0.7525	−1.558	0.986
79.8	0.7351	−0.936	1.026	0.7448	−1.301	0.993	0.7540	−1.538	0.969
119.7	0.7381	−0.913	0.988	0.7477	−1.269	0.961	0.7569	−1.501	0.938
159.6	0.7409	−0.889	0.952	0.7505	−1.239	0.932	0.7597	−1.465	0.910
199.5	0.7437	−0.866	0.918	0.7533	−1.210	0.905	0.7624	−1.431	0.884
239.3	0.7464	−0.841	0.888	0.7560	−1.183	0.881	0.7651	−1.400	0.861
289.2	0.7496	−0.811	0.853	0.7592	−1.151	0.853	0.7683	−1.363	0.834
339.0	0.7528	−0.779	0.822	0.7624	−1.121	0.829	0.7715	−1.328	0.811
		$x_1 = 0.4992$			$x_1 = 0.5503$			$x_1 = 0.5994$	
1.0	0.7572	−1.734	1.008	0.7616	−1.734	1.007	0.7657	−1.695	1.019
20.0	0.7586	−1.711	0.992	0.7631	−1.711	0.991	0.7671	−1.675	1.002
59.9	0.7616	−1.664	0.960	0.7660	−1.666	0.960	0.7702	−1.633	0.970
79.8	0.7631	−1.643	0.945	0.7675	−1.645	0.945	0.7716	−1.614	0.954
119.7	0.7659	−1.601	0.916	0.7703	−1.605	0.918	0.7745	−1.576	0.925
159.6	0.7687	−1.562	0.891	0.7731	−1.567	0.893	0.7774	−1.541	0.898
199.5	0.7714	−1.525	0.867	0.7759	−1.532	0.871	0.7801	−1.508	0.874
239.3	0.7740	−1.491	0.846	0.7785	−1.499	0.850	0.7828	−1.477	0.852
289.2	0.7772	−1.451	0.822	0.7818	−1.462	0.827	0.7861	−1.441	0.827
339.0	0.7804	−1.415	0.801	0.7850	−1.429	0.807	0.7893	−1.408	0.804
		$x_1 = 0.7010$			$x_1 = 0.8010$			$x_1 = 0.8991$	
1.0	0.7733	−1.496	1.006	0.7794	−1.142	1.046	0.7839	−0.648	1.110
20.0	0.7747	−1.475	0.990	0.7809	−1.127	1.030	0.7855	−0.640	1.090
59.9	0.7777	−1.435	0.960	0.7841	−1.097	0.998	0.7889	−0.624	1.050
79.8	0.7792	−1.415	0.946	0.7857	−1.083	0.983	0.7905	−0.616	1.030
119.7	0.7821	−1.379	0.919	0.7887	−1.057	0.955	0.7937	−0.601	0.994
159.6	0.7849	−1.345	0.894	0.7917	−1.033	0.929	0.7968	−0.586	0.959
199.5	0.7877	−1.314	0.872	0.7946	−1.011	0.905	0.7998	−0.572	0.927
289.2	0.7937	−1.253	0.829	0.8009	−0.969	0.858	0.8063	−0.541	0.861
339.0	0.7970	−1.224	0.809	0.8043	−0.950	0.835	0.8097	−0.524	0.828
		$x_1 = 0.9499$			$x_1 = 1.0000$				
1.0	0.7855	−0.339	1.146	0.7866	0.000	1.191			
20.0	0.7872	−0.335	1.125	0.7884	0.000	1.170			
59.9	0.7907	−0.326	1.085	0.7920	0.000	1.128			
79.8	0.7924	−0.322	1.065	0.7938	0.000	1.107			
119.7	0.7957	−0.314	1.028	0.7972	0.000	1.068			
159.6	0.7989	−0.306	0.993	0.8006	0.000	1.032			
199.5	0.8021	−0.299	0.960	0.8038	0.000	0.997			
239.3	0.8051	−0.292	0.929	0.8070	0.000	0.965			
289.2	0.8088	−0.233	0.893	0.8108	0.000	0.926			
339.0	0.8123	−0.275	0.860	0.8145	0.000	0.890			

Table 3. Experimental Densities, Excess Volumes, and Compressibilities for the System Ethanol (1) + Propylamine (2) at 298.15 K

P/bar	ρ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}	ρ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}	ρ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}
		$x_1 = 0.0511$			$x_1 = 0.1099$			$x_1 = 0.2044$	
1.0	0.7159	−0.224	1.1	0.7214	−0.465	1.133	0.7301	−0.802	1.099
20.0	0.7175	−0.222	1.1	0.7229	−0.459	1.113	0.7316	−0.791	1.080
59.9	0.7207	−0.216	1.0	0.7261	−0.447	1.072	0.7347	−0.771	1.041
79.8	0.72222	−0.213	1.0	0.7276	−0.441	1.053	0.7362	−0.761	1.023
119.7	0.7253	−0.208	1.0	0.7306	−0.430	1.017	0.7392	−0.741	0.990
159.6	0.7282	−0.203	1.0	0.7335	−0.419	0.985	0.7421	−0.723	0.959
199.5	0.7311	−0.197	0.9	0.7364	−0.409	0.955	0.7449	−0.706	0.931
239.3	0.7339	−0.192	0.9	0.7391	−0.399	0.928	0.7476	−0.690	0.905
289.2	0.7373	−0.186	0.9	0.7425	−0.386	0.898	0.7509	−0.670	0.877
339.0	0.7407	−0.181	0.8	0.7458	−0.375	0.871	0.7542	−0.652	0.851
		$x_1 = 0.3037$			$x_1 = 0.4073$			$x_1 = 0.5022$	
1.0	0.7392	−1.077	1.072	0.7483	−1.264	1.051	0.7563	−1.337	1.031
20.0	0.7407	−1.063	1.053	0.7498	−1.248	1.032	0.7577	−1.321	1.014
59.9	0.7437	−1.036	1.016	0.7529	−1.218	0.995	0.7608	−1.288	0.979
79.8	0.7452	−1.023	0.998	0.7543	−1.203	0.978	0.7622	−1.272	0.963
119.7	0.7481	−0.998	0.966	0.7572	−1.175	0.945	0.7651	−1.243	0.933
159.6	0.7510	−0.974	0.936	0.7601	−1.147	0.915	0.7679	−1.215	0.905
199.5	0.7538	−0.952	0.908	0.7628	−1.121	0.887	0.7707	−1.188	0.879
239.3	0.7565	−0.931	0.884	0.7655	−1.095	0.862	0.7733	−1.163	0.856
289.2	0.7598	−0.905	0.856	0.7687	−1.065	0.834	0.7766	−1.134	0.829
339.0	0.7630	−0.881	0.831	0.7719	−1.036	0.808	0.7798	−1.106	0.806

Table 3 (Continued)

P/bar	ϱ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}	ϱ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}	ϱ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}
		$x_1 = 0.5516$			$x_1 = 0.6049$			$x_1 = 0.7015$	
1.0	0.7602	−1.336	1.027	0.7642	−1.303	1.021	0.7709	−1.160	1.018
20.0	0.7617	−1.320	1.010	0.7657	−1.287	1.003	0.7724	−1.146	1.001
59.9	0.7647	−1.288	0.974	0.7687	−1.256	0.968	0.7755	−1.117	0.969
79.8	0.7662	−1.272	0.958	0.7702	−1.240	0.952	0.7769	−1.104	0.953
119.7	0.7691	−1.243	0.927	0.7731	−1.211	0.920	0.7799	−1.079	0.924
159.6	0.7719	−1.214	0.898	0.7759	−1.182	0.892	0.7827	−1.055	0.898
199.5	0.7746	−1.187	0.872	0.7786	−1.155	0.865	0.7855	−1.033	0.874
239.3	0.7773	−1.162	0.848	0.7812	−1.129	0.841	0.7882	−1.013	0.851
289.2	0.7805	−1.131	0.821	0.7845	−1.098	0.813	0.7915	−0.989	0.826
339.0	0.7837	−1.102	0.797	0.7876	−1.069	0.788	0.7947	−0.968	0.803
		$x_1 = 0.8013$			$x_1 = 0.8969$			$x_1 = 0.9502$	
1.0	0.7769	−0.894	1.022	0.7815	−0.525	1.034	0.7836	−0.269	1.054
20.0	0.7784	−0.882	1.005	0.7830	−0.517	1.018	0.7851	−0.265	1.037
59.9	0.7815	−0.859	0.971	0.7862	−0.502	0.986	0.7883	−0.258	1.002
79.8	0.7830	−0.848	0.955	0.7877	−0.495	0.970	0.7899	−0.254	0.986
119.7	0.7859	−0.827	0.925	0.7907	−0.482	0.941	0.7930	−0.247	0.955
159.6	0.7888	−0.808	0.897	0.7937	−0.471	0.915	0.7960	−0.241	0.927
199.5	0.7916	−0.789	0.872	0.7965	−0.460	0.890	0.7989	−0.236	0.900
239.3	0.7943	−0.772	0.848	0.7993	−0.451	0.868	0.8017	−0.231	0.876
289.2	0.7976	−0.752	0.821	0.8027	−0.442	0.842	0.8052	−0.226	0.847
339.0	0.8008	−0.733	0.796	0.8061	−0.434	0.818	0.8085	−0.222	0.821
		$x_1 = 1.0000$							
1.0	0.7852	0.000	1.079						
20.0	0.7868	0.000	1.061						
59.9	0.7900	0.000	1.024						
79.8	0.7916	0.000	1.006						
119.7	0.7948	0.000	0.973						
159.6	0.7978	0.000	0.942						
199.5	0.8008	0.000	0.913						
239.3	0.8036	0.000	0.886						
289.2	0.8071	0.000	0.854						
339.0	0.8105	0.000	0.825						

Table 4. Experimental Densities, Excess Volumes, and Compressibilities for the System 1-Propanol (1) + Propylamine (2) at 298.15 K

P/bar	ϱ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}	ϱ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}	ϱ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}
		$x_1 = 0.0500$			$x_1 = 0.1049$			$x_1 = 0.2043$	
1.0	0.7169	−0.187	1.1	0.7232	−0.397	1.113	0.7347	−0.755	1.061
20.0	0.7184	−0.183	1.1	0.7247	−0.390	1.094	0.7362	−0.743	1.042
59.9	0.7216	−0.176	1.0	0.7278	−0.377	1.057	0.7392	−0.719	1.005
79.8	0.7231	−0.173	1.0	0.7294	−0.372	1.040	0.7406	−0.707	0.988
119.7	0.7262	−0.167	1.0	0.7323	−0.361	1.008	0.7435	−0.684	0.955
159.6	0.7291	−0.163	1.0	0.7352	−0.352	0.979	0.7463	−0.662	0.925
199.5	0.7320	−0.159	0.9	0.7381	−0.343	0.953	0.7490	−0.641	0.898
239.3	0.7348	−0.156	0.9	0.7409	−0.336	0.929	0.7517	−0.621	0.874
289.2	0.7382	−0.154	0.9	0.7443	−0.329	0.903	0.7549	−0.597	0.846
339.0	0.7416	−0.153	0.8	0.7476	−0.324	0.880	0.7581	−0.573	0.822
		$x_1 = 0.3053$			$x_1 = 0.4099$			$x_1 = 0.5069$	
1.0	0.7461	−1.050	1.029	0.7572	−1.248	0.996	0.7665	−1.315	0.964
20.0	0.7475	−1.036	1.011	0.7586	−1.232	0.979	0.7679	−1.298	0.948
59.9	0.7505	−1.008	0.976	0.7615	−1.202	0.948	0.7708	−1.264	0.918
79.8	0.7519	−0.995	0.960	0.7629	−1.187	0.933	0.7722	−1.248	0.904
119.7	0.7548	−0.969	0.929	0.7657	−1.159	0.905	0.7749	−1.217	0.877
159.6	0.7575	−0.944	0.901	0.7685	−1.133	0.880	0.7776	−1.188	0.853
199.5	0.7602	−0.920	0.876	0.7711	−1.108	0.857	0.7802	−1.161	0.831
239.3	0.7629	−0.898	0.853	0.7737	−1.085	0.837	0.7828	−1.136	0.812
289.2	0.7661	−0.871	0.827	0.7769	−1.059	0.814	0.7859	−1.106	0.790
339.0	0.7692	−0.845	0.804	0.7800	−1.034	0.794	0.7890	−1.078	0.770
		$x_1 = 0.5501$			$x_1 = 0.6023$			$x_1 = 0.7038$	
1.0	0.7704	−1.307	0.957	0.7748	−1.265	0.946	0.7825	−1.089	0.942
20.0	0.7718	−1.291	0.942	0.7762	−1.249	0.932	0.7839	−1.076	0.927
59.9	0.7747	−1.259	0.914	0.7790	−1.218	0.904	0.7867	−1.051	0.898
79.8	0.7761	−1.243	0.900	0.7804	−1.203	0.891	0.7881	−1.039	0.884
119.7	0.7788	−1.215	0.875	0.7832	−1.175	0.867	0.7909	−1.016	0.858
159.6	0.7815	−1.188	0.852	0.7858	−1.149	0.845	0.7936	−0.994	0.835
199.5	0.7841	−1.163	0.832	0.7885	−1.125	0.825	0.7962	−0.973	0.813
239.3	0.7867	−1.140	0.813	0.7910	−1.104	0.808	0.7987	−0.954	0.793
289.2	0.7899	−1.114	0.792	0.7942	−1.079	0.788	0.8019	−0.931	0.771
339.0	0.7930	−1.090	0.774	0.7973	−1.058	0.771	0.8049	−0.909	0.752
		$x_1 = 0.8070$			$x_1 = 0.9135$			$x_1 = 0.9520$	
1.0	0.7892	−0.791	0.935	0.7952	−0.383	0.938	0.7972	−0.217	0.940
20.0	0.7906	−0.782	0.921	0.7966	−0.379	0.923	0.7986	−0.214	0.925
59.9	0.7935	−0.764	0.892	0.7995	−0.370	0.893	0.8015	−0.210	0.896
79.8	0.7949	−0.755	0.879	0.8009	−0.366	0.879	0.8029	−0.207	0.882
119.7	0.7976	−0.738	0.853	0.8037	−0.357	0.853	0.8057	−0.203	0.856
159.6	0.8003	−0.722	0.830	0.8064	−0.349	0.829	0.8084	−0.198	0.832
199.5	0.8029	−0.707	0.809	0.8090	−0.340	0.806	0.8111	−0.194	0.810
239.3	0.8055	−0.692	0.789	0.8116	−0.332	0.785	0.8137	−0.189	0.790
289.2	0.8086	−0.676	0.767	0.8147	−0.322	0.762	0.8168	−0.184	0.767
339.0	0.8117	−0.660	0.748	0.8178	−0.312	0.741	0.8199	−0.179	0.746

Table 4 (Continued)

P/bar	ϱ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}	ϱ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}	ϱ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}
		$x_1 = 1.0000$							
1.0	0.7995	0.000	0.942						
20.0	0.8010	0.000	0.927						
59.9	0.8039	0.000	0.898						
79.8	0.8053	0.000	0.885						
119.7	0.8081	0.000	0.859						
159.6	0.8109	0.000	0.835						
199.5	0.8135	0.000	0.813						
239.3	0.8161	0.000	0.793						
289.2	0.8193	0.000	0.770						
339.0	0.8224	0.000	0.749						

Table 5. Experimental Densities, Excess Volumes, and Compressibilities for the System 1-Butanol (1) + Propylamine (2) at 298.15 K

P/bar	ϱ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}	ϱ/(g·cm^{-3})	V_E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}	ϱ/(g·cm^{-3})	V_E/(cm^3·mol^{-1})	$10^4\beta_T$/bar^{-1}
		$x_1 = 0.0489$			$x_1 = 0.0992$			$x_1 = 0.2046$	
1.0	0.7179	−0.184	1.14	0.7247	−0.371	1.113	0.7386	−0.730	1.053
20.0	0.7195	−0.181	1.12	0.7263	−0.365	1.093	0.7400	−0.720	1.034
59.9	0.7226	−0.175	1.08	0.7294	−0.354	1.053	0.7430	−0.699	0.998
79.8	0.7242	−0.172	1.06	0.7309	−0.349	1.035	0.7445	−0.689	0.982
119.7	0.7272	−0.167	1.02	0.7339	−0.339	1.000	0.7474	−0.669	0.950
159.6	0.7301	−0.162	0.99	0.7367	−0.329	0.968	0.7502	−0.651	0.922
199.5	0.7330	−0.156	0.96	0.7396	−0.319	0.938	0.7529	−0.634	0.896
239.3	0.7358	−0.151	0.93	0.7423	−0.309	0.912	0.7556	−0.617	0.872
289.2	0.7392	−0.145	0.90	0.7456	−0.297	0.882	0.7588	−0.597	0.846
339.0	0.7425	−0.139	0.87	0.7489	−0.285	0.856	0.7620	−0.579	0.823
		$x_1 = 0.3022$			$x_1 = 0.3978$			$x_1 = 0.4999$	
1.0	0.7506	−0.996	1.009	0.7615	−1.170	0.978	0.7719	−1.244	0.933
20.0	0.7520	−0.983	0.992	0.7629	−1.156	0.961	0.7733	−1.227	0.919
59.9	0.7550	−0.956	0.958	0.7658	−1.127	0.929	0.7761	−1.194	0.892
79.8	0.7564	−0.943	0.943	0.7672	−1.113	0.914	0.7775	−1.179	0.879
119.7	0.7592	−0.919	0.913	0.7700	−1.087	0.885	0.7801	−1.150	0.856
159.6	0.7619	−0.895	0.887	0.7726	−1.062	0.859	0.7828	−1.123	0.835
199.5	0.7646	−0.873	0.863	0.7753	−1.037	0.836	0.7854	−1.099	0.815
239.3	0.7672	−0.853	0.841	0.7778	−1.014	0.814	0.7879	−1.077	0.798
289.2	0.7704	−0.828	0.816	0.7809	−0.986	0.790	0.7910	−1.052	0.780
339.0	0.7735	−0.805	0.795	0.7840	−0.960	0.769	0.7940	−1.030	0.764
		$x_1 = 0.5489$			$x_1 = 0.6033$			$x_1 = 0.6587$	
1.0	0.7765	−1.237	0.926	0.7812	−1.195	0.927	0.7856	−1.1174	0.887
20.0	0.7778	−1.221	0.912	0.7825	−1.182	0.912	0.7869	−1.1009	0.876
59.9	0.7806	−1.190	0.885	0.7853	−1.156	0.882	0.7896	−1.0690	0.854
79.8	0.7820	−1.176	0.872	0.7867	−1.143	0.868	0.7909	−1.0543	0.844
119.7	0.7847	−1.148	0.848	0.7894	−1.119	0.841	0.7936	−1.0276	0.825
159.6	0.7873	−1.123	0.826	0.7920	−1.095	0.817	0.7962	−1.0042	0.808
199.5	0.7899	−1.099	0.806	0.7946	−1.072	0.795	0.7987	−0.9840	0.794
239.3	0.7924	−1.077	0.788	0.7971	−1.050	0.774	0.8012	−0.9669	0.781
289.2	0.7955	−1.052	0.768	0.8001	−1.023	0.752	0.8043	−0.9497	0.767
339.0	0.7985	−1.029	0.751	0.8031	−0.997	0.731	0.8074	−0.9369	0.756
		$x_1 = 0.7039$			$x_1 = 0.8017$			$x_1 = 0.8998$	
1.0	0.7889	−1.028	0.899	0.7953	−0.763	0.892	0.8009	−0.414	0.884
20.0	0.7902	−1.015	0.886	0.7967	−0.754	0.878	0.8022	−0.408	0.871
59.9	0.7930	−0.990	0.858	0.7994	−0.736	0.851	0.8050	−0.398	0.844
79.8	0.7943	−0.978	0.845	0.8008	−0.727	0.838	0.8063	−0.393	0.831
119.7	0.7970	−0.955	0.821	0.8034	−0.711	0.814	0.8089	−0.383	0.807
159.6	0.7996	−0.933	0.799	0.8060	−0.695	0.792	0.8115	−0.373	0.785
199.5	0.8021	−0.913	0.779	0.8085	−0.679	0.772	0.8140	−0.363	0.765
239.3	0.8046	−0.893	0.761	0.8110	−0.665	0.754	0.8165	−0.354	0.747
289.2	0.8076	−0.870	0.741	0.8140	−0.647	0.733	0.8195	−0.343	0.726
339.0	0.8105	−0.848	0.723	0.8169	−0.630	0.715	0.8224	−0.332	0.708
		$x_1 = 0.9511$			$x_1 = 1.0000$				
1.0	0.8035	−0.207	0.886	0.8059	0.000	0.884			
20.0	0.8048	−0.205	0.872	0.8072	0.000	0.871			
59.9	0.8076	−0.200	0.845	0.8100	0.000	0.845			
79.8	0.8090	−0.197	0.832	0.8113	0.000	0.832			
119.7	0.8116	−0.193	0.808	0.8140	0.000	0.809			
159.6	0.8142	−0.187	0.786	0.8166	0.000	0.788			
199.5	0.8167	−0.182	0.765	0.8191	0.000	0.768			
239.3	0.8192	−0.177	0.746	0.8216	0.000	0.750			
289.2	0.8222	−0.170	0.725	0.8247	0.000	0.730			
339.0	0.8251	−0.163	0.706	0.8276	0.000	0.712			

principle, and the working equations have been described previously (*4*). For reference purposes the viscosity at atmospheric pressure was measured with two Ubbelohde viscometers with precisely known constants. The viscosity coefficients are estimated to be measured with an accuracy better than ±1% in the range of pressures up to 400 bar and better than 2.5% for higher pressures (*4*).

Results

For each binary mixture we have conducted measurements of density, ϱ, at 12 intermediate compositions (plus the 2 pure components) and at 30 pressures, P, from atmospheric to 340 bar, for each composition. From these density results the isothermal compressibility, β, and the

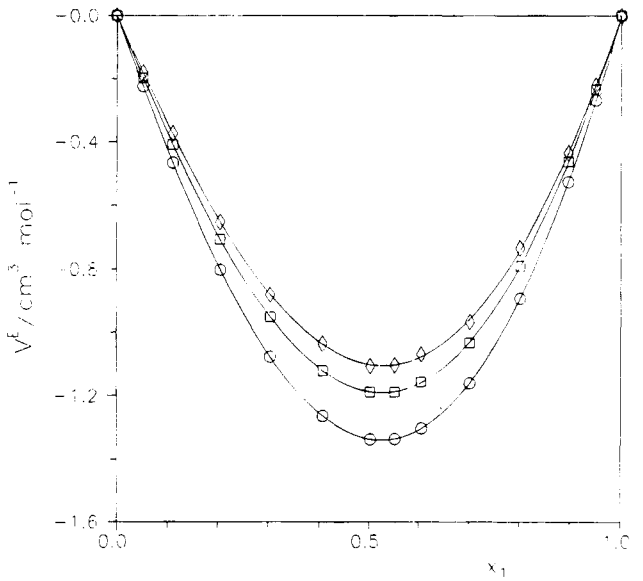

Figure 2. Excess volume for the system ethanol (1) + propylamine (2) at 298.15 K: ○, P = 1.01 bar; □, P = 199.5 bar, ◇, P = 339.0 bar; —, eq 2.

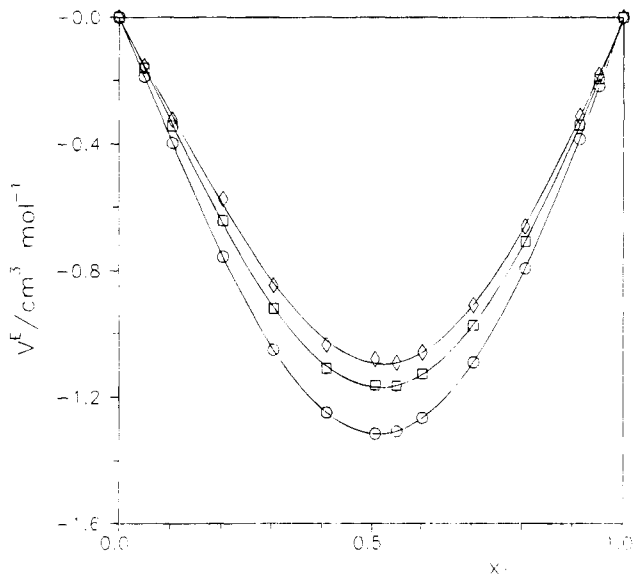

Figure 3. Excess volume for the system 1-propanol (1) + propylamine (2) at 298.15 K: ○, P = 1.01 bar; □, P = 199.5 bar, ◇, P = 339.0 bar; —, eq 2.

excess volume, V^E, were calculated. For a mixture of components 1 and 2, V^E is defined by

$$V^E = V - x_1V_1 - x_2V_2 = x_1M_1\left(\frac{1}{\varrho} - \frac{1}{\varrho_1}\right) + x_2M_2\left(\frac{1}{\varrho} - \frac{1}{\varrho_2}\right) \quad (1)$$

where M_i and V_i are the molar mass and volume, respectively, of component i. In Tables 2–5 are reported the experimental densities of the four binary mixtures at 25 °C along with the calculated excess volume and the isothermal compressibility. Results are reported at 10 pressures for each composition. The full tables with data at all pressures and compositions are available upon request from the authors.

In Figures 1–4 are shown the experimental excess volumes at three pressures for the four binary mixtures. The solid lines were calculated by fitting the experimental

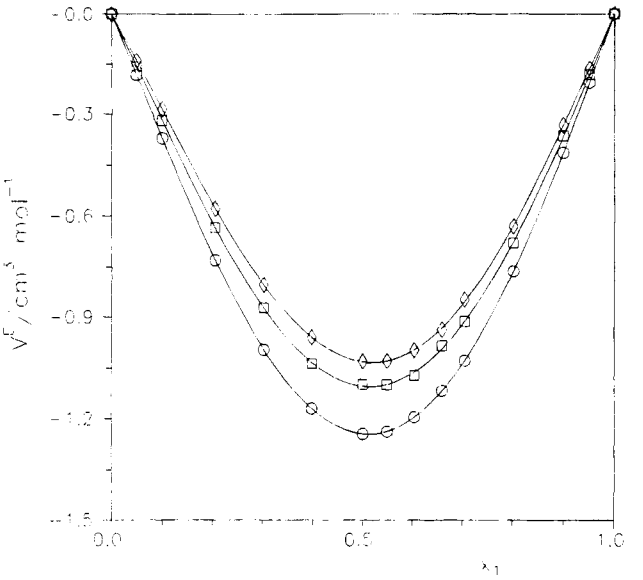

Figure 4. Excess volume for the system 1-butanol (1) + propylamine (2) at 298.15 K: ○, P = 1.01 bar; □, P = 199.5 bar, ◇, P = 339.0 bar; —, eq 2.

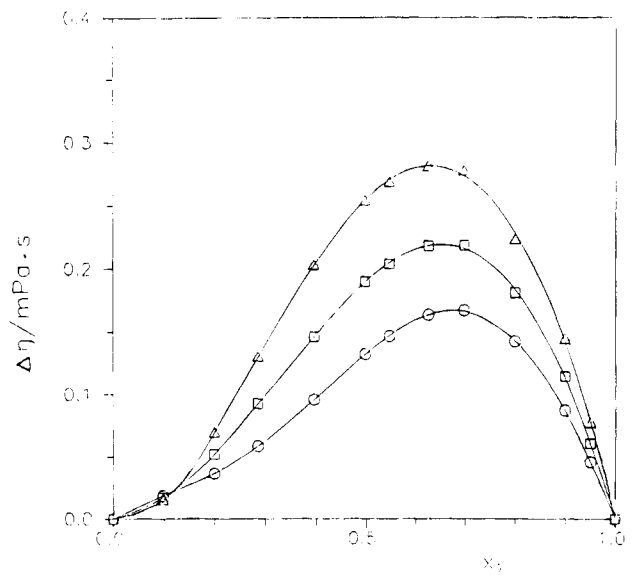

Figure 5. Viscosity deviation for the system methanol (1) + propylamine (2) at 298.15 K: ○, P = 1.01 bar; □, P = 244.1 bar; △, P = 518.0 bar; —, eq 4.

data to a Redlich–Kister-type equation:

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1x_2\sum_{j=0}^{n} v_j(2x_1 - 1)^j \quad (2)$$

The coefficients v_j along with the standard deviation of fit (% AAD = $100x\sum_{i=1}^{N}\{(V^E_{i,\text{exp}} - V^E_{i,\text{calc}})/V^E_{i,\text{exp}}\}/N$, N being the number of experimental data) are reported in Table 6.

For each binary system viscosity measurements were made at 11 or 12 intermediate compositions (plus 2 for the pure components) and at 12 pressures from atmospheric to 520 bar, for each composition. These experimental viscosities are reported in Tables 7–10. From these data on viscosities one can calculate the viscosity deviation of the mixture defined by

$$\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2 \quad (3)$$

In Figures 5–8 are shown the experimental viscosity deviations of the four binary mixtures at three pressures.

Table 6. Coefficients v_j of Eq 2 and Percent Average Absolute Deviation of Fit (% AAD)

	P = 1.013 bar	P = 199.5 bar	P = 339.0 bar
	Methanol (1) + Propylamine (2)		
v_0	−6.9369	−6.1295	−5.6966
v_1	−0.7642	−0.6867	−0.7403
v_2	0.6940	0.6401	0.6386
v_3	−0.1029	−0.0590	−0.0192
v_4	0.0208	−0.0219	0.1232
% AAD	0.0128	0.1819	0.6748
	Ethanol (1) + Propylamine (2)		
v_0	−5.3464	−4.7482	−4.4055
v_1	−0.5567	−0.5326	−0.5262
v_2	0.2119	0.2465	0.2094
v_3	−0.0468	0.0315	−0.0118
v_4	0.0117	0.0431	0.0572
% AAD	0.0089	0.1114	0.3222
	1-Propanol (1) + Propylamine (2)		
v_0	−5.2587	−4.6687	−4.3655
v_1	−0.3372	−0.4244	−0.5574
v_2	1.0889	1.1647	1.4381
v_3	−0.1407	−0.0988	0.1796
v_4	0.0310	−0.1237	−0.5886
% AAD	0.0090	0.4351	0.9246
	1-Butanol (1) + Propylamine (2)		
v_0	−4.9771	−4.4193	−4.1284
v_1	−0.2703	−0.3005	−0.3872
v_2	0.9193	0.9767	1.0248
v_3	−0.0084	−0.0126	0.1207
v_4	0.0364	−0.0402	0.0572
% AAD	0.0029	0.2862	0.1486

The solid lines were calculated by fitting the results to the Redlich–Kister-type equation

$$\Delta\eta/(\text{mPa·s}) = x_1x_2\sum_{j=0}^{n} h_j(2x_1 - 1)^j \qquad (4)$$

The coefficients h_j along with the standard deviation of fit are reported in Table 11.

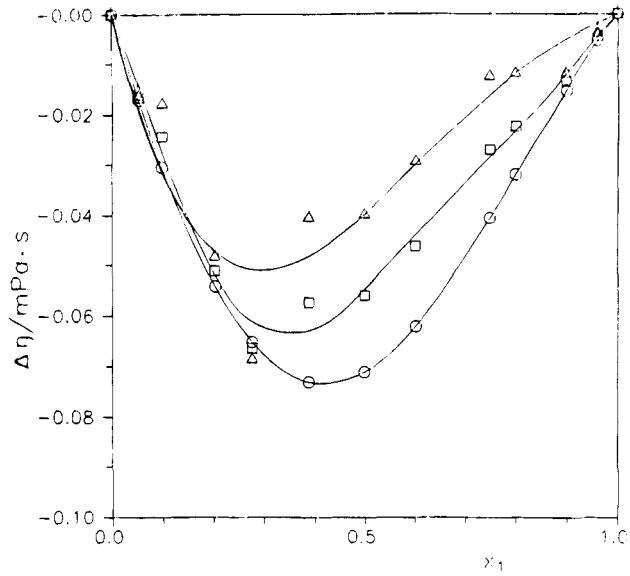

Figure 6. Viscosity deviation for the system ethanol (1) + propylamine (2) at 298.15 K: ○, P = 1.01 bar; □, P = 244.1 bar; △, P = 518.0 bar; —, eq 4.

Discussion

Before discussing the properties of binary mixtures, it is worth comparing the properties of the pure components. From Tables 2–5 and 7–10, propylamine and methanol have similar isothermal compressibilities and their viscosities are not remarkably different. The compressibilities of the other alkanols are smaller and decrease as the chain length of the alkanol molecule increases. The increase of the viscosity with the chain length is much more pronounced: the viscosity of 1-propanol is about 5 times larger than the viscosity of propylamine although their sizes are similar; the viscosity of butanol is almost an order of magnitude larger than the viscosity of propylamine al-

Table 7. Experimental Viscosities for the System Methanol (1) + Propylamine (2) at 298.15 K

	η/(mPa·s)												
P/bar	x_1 = 0.0000	x_1 = 0.0987	x_1 = 0.1995	x_1 = 0.2868	x_1 = 0.3970	x_1 = 0.4985	x_1 = 0.5475	x_1 = 0.6249	x_1 = 0.6977	x_1 = 0.8000	x_1 = 0.8982	x_1 = 0.9499	x_1 = 1.000
1.0	0.3650	0.4013	0.4374	0.4756	0.5323	0.5872	0.6104	0.6414	0.6580	0.6520	0.6144	0.5827	0.5457
44.7	0.3781	0.4140	0.4529	0.4941	0.5536	0.6095	0.6326	0.6630	0.6788	0.6701	0.6303	0.5963	0.5566
94.6	0.3931	0.4284	0.4707	0.5153	0.5779	0.6349	0.6580	0.6877	0.7027	0.6909	0.6485	0.6118	0.5689
144.4	0.4082	0.4429	0.4885	0.5365	0.6023	0.6605	0.6834	0.7125	0.7266	0.7117	0.6668	0.6274	0.5814
194.3	0.4233	0.4575	0.5063	0.5577	0.6267	0.6860	0.7089	0.7373	0.7506	0.7326	0.6851	0.6431	0.5939
244.1	0.4385	0.4721	0.5242	0.5790	0.6512	0.7117	0.7344	0.7622	0.7746	0.7535	0.7034	0.6588	0.6064
294.0	0.4537	0.4867	0.5421	0.6004	0.6758	0.7374	0.7599	0.7872	0.7986	0.7745	0.7218	0.6746	0.6190
343.8	0.4690	0.5014	0.5600	0.6218	0.7004	0.7631	0.7856	0.8122	0.8228	0.7955	0.7403	0.6904	0.6316
393.6	0.4843	0.5161	0.5781	0.6432	0.7250	0.7889	0.8113	0.8373	0.8469	0.8166	0.7588	0.7062	0.6442
443.5	0.4997	0.5309	0.5961	0.6647	0.7497	0.8148	0.8370	0.8624	0.8712	0.8377	0.7774	0.7221	0.6569
493.4	0.5151	0.5457	0.6142	0.6863	0.7745	0.8407	0.8628	0.8876	0.8955	0.8589	0.7960	0.7381	0.6694
518.0	0.5227	0.5531	0.6232	0.6970	0.7868	0.8536	0.8756	0.9001	0.9075	0.8694	0.8053	0.7460	0.6760

Table 8. Experimental Viscosities for the System Ethanol (1) + Propylamine (2) at 298.15 K

	η/(mPa·s)											
P/bar	x_1 = 0.0515	x_1 = 0.0980	x_1 = 0.2026	x_1 = 0.2763	x_1 = 0.3874	x_1 = 0.4986	x_1 = 0.6013	x_1 = 0.7485	x_1 = 0.7991	x_1 = 0.8981	x_1 = 0.961	x_1 = 1.000
1.0	0.3851	0.4053	0.4571	0.4993	0.5717	0.6539	0.7371	0.8650	0.9101	0.9984	1.052	1.0870
44.7	0.3993	0.4213	0.4745	0.5174	0.5949	0.6791	0.7643	0.8945	0.9399	1.0286	1.0841	1.1188
94.6	0.4156	0.4397	0.4945	0.5380	0.6214	0.7078	0.7954	0.9283	0.9740	1.0632	1.1197	1.1551
144.4	0.4319	0.4581	0.5145	0.5588	0.6480	0.7367	0.8266	0.9621	1.0081	1.0978	1.1554	1.1915
194.3	0.4482	0.4766	0.5346	0.5795	0.6746	0.7656	0.8578	0.9960	1.0423	1.1325	1.1913	1.2281
244.1	0.4646	0.4951	0.5547	0.6004	0.7013	0.7945	0.8891	1.0300	1.0766	1.1673	1.2273	1.2647
294.0	0.4810	0.5137	0.5749	0.6212	0.7280	0.8235	0.9205	1.0641	1.1110	1.2023	1.2634	1.3015
343.8	0.4975	0.5324	0.5951	0.6422	0.7548	0.8526	0.9519	1.0983	1.1455	1.2373	1.2995	1.3384
393.6	0.5140	0.5510	0.6154	0.6631	0.7816	0.8817	0.9834	1.1325	1.1801	1.2724	1.3358	1.3754
443.5	0.5306	0.5698	0.6357	0.6842	0.8085	0.9110	1.0150	1.1669	1.2148	1.3076	1.3723	1.4125
493.4	0.5472	0.5886	0.6561	0.7052	0.8355	0.9402	1.0467	1.2013	1.2496	1.3429	1.4088	1.4498
518.0	0.5555	0.5979	0.6662	0.7157	0.8489	0.9547	1.0624	1.2184	1.2668	1.3604	1.4269	1.4683

Table 9. Experimental Viscosities for the System 1-Propanol (1) + Propylamine (2) at 298.15 K

	η/(mPa·s)											
P/bar	x_1 = 0.0523	x_1 = 0.1008	x_1 = 0.2001	x_1 = 0.2985	x_1 = 0.3979	x_1 = 0.5037	x_1 = 0.5989	x_1 = 0.7015	x_1 = 0.7962	x_1 = 0.9032	x_1 = 0.9626	x_1 = 1.000
1.0	0.3938	0.4276	0.5072	0.6113	0.7332	0.8640	1.0025	1.1860	1.3777	1.6705	1.8433	1.9680
44.7	0.4069	0.4418	0.5266	0.6368	0.7649	0.9031	1.0477	1.2352	1.4311	1.7320	1.9102	2.0395
94.6	0.4218	0.4580	0.5487	0.6660	0.8012	0.9479	1.0995	1.2916	1.4922	1.8023	1.9867	2.1212
144.4	0.4368	0.4742	0.5709	0.6952	0.8375	0.9928	1.1513	1.3481	1.5535	1.8728	2.0635	2.2031
194.3	0.4518	0.4905	0.5931	0.7245	0.8738	1.3078	1.2032	1.4047	1.6149	1.9435	2.1405	2.2854
244.1	0.4669	0.5068	0.6154	0.7539	0.9103	1.0828	1.2552	1.4614	1.6765	2.0144	2.2178	2.3679
294.0	0.4820	0.5232	0.6378	0.7833	0.9467	1.1280	1.3073	1.5184	1.7382	2.0856	2.2953	2.4507
343.8	0.4971	0.5396	0.6602	0.8128	0.9833	1.1733	1.3596	1.5754	1.8002	2.1569	2.3731	2.5338
393.6	0.5123	0.5561	0.6826	0.8424	1.0199	1.2186	1.4119	1.6326	1.8623	2.2285	2.4512	2.6171
443.5	0.5276	0.5726	0.7051	0.8720	1.0567	1.2641	1.4644	1.6900	1.9246	2.3003	2.5294	2.7007
493.4	0.5429	0.5891	0.7276	0.9016	1.0934	1.3096	1.5170	1.7475	1.9870	2.3723	2.6080	2.7846
518.0	0.5504	0.5973	0.7388	0.9164	1.1117	1.3322	1.5431	1.7760	2.0180	2.4080	2.6470	2.8263

Table 10. Experimental Viscosities for the System 1-Butanol (1) + Propylamine (2) at 298.15 K

	η/(mPa·s)											
P/bar	x_1 = 0.0488	x_1 = 0.0977	x_1 = 0.2026	x_1 = 0.2966	x_1 = 0.4000	x_1 = 0.4939	x_1 = 0.5800	x_1 = 0.6450	x_1 = 0.7024	x_1 = 0.7958	x_1 = 0.9025	x_1 = 1.000
1.0	0.3946	0.4367	0.5520	0.6772	0.8384	1.0033	1.1663	1.3050	1.4495	1.7211	2.1134	2.5780
44.7	0.4092	0.4355	0.5762	0.7091	0.8779	1.0488	1.2175	1.3606	1.5087	1.7891	2.1985	2.6904
94.6	0.4258	0.4728	0.6038	0.7456	0.9231	1.1009	1.2760	1.4242	1.5764	1.8668	2.2960	2.8190
144.4	0.4425	0.4921	0.6315	0.7821	0.9684	1.1531	1.3347	1.4879	1.6444	1.9448	2.3938	2.9480
194.3	0.4593	0.5114	0.6593	0.8187	1.0138	1.2054	1.3935	1.5518	1.7125	2.0230	2.4919	3.0775
244.1	0.4761	0.5308	0.6871	0.8553	1.0593	1.2578	1.4525	1.6159	1.7808	2.1014	2.5903	3.2073
294.0	0.4929	0.5503	0.7150	0.8920	1.1048	1.3103	1.5116	1.6800	1.8493	2.1800	2.6890	3.3376
343.8	0.5098	0.5698	0.7429	0.9287	1.1505	1.3629	1.5709	1.7444	1.9180	2.2589	2.7880	3.4684
393.6	0.5268	0.5893	0.7709	0.9655	1.1962	1.4156	1.6303	1.8089	1.9869	2.3380	2.8873	3.5995
443.5	0.5437	0.6089	0.7989	1.0024	1.2421	1.4685	1.6899	1.8737	2.0560	2.4174	2.9870	3.7311
493.4	0.5608	0.6286	0.8270	1.0394	1.2880	1.5215	1.7496	1.9385	2.1252	2.4970	3.0869	3.8632
518.0	0.5692	0.6383	0.8409	1.0577	1.3108	1.5478	1.7792	1.9708	2.1596	2.5365	3.1366	3.9287

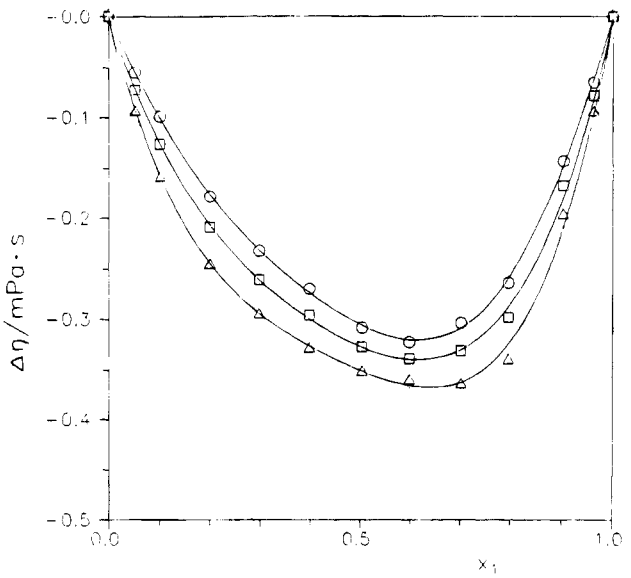

Figure 7. Viscosity deviation for the system 1-propanol (1) + propylamine (2) at 298.15 K: ○, P = 1.01 bar; □, P = 244.1 bar; △, P = 518.0 bar; —, eq 4.

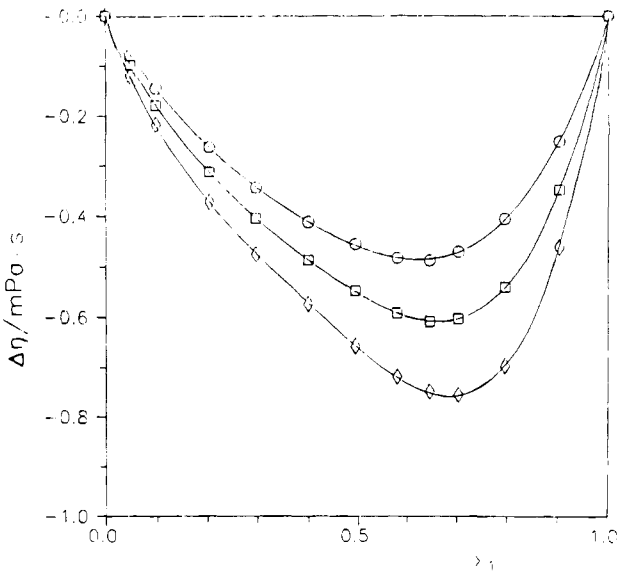

Figure 8. Viscosity deviation for the system 1-butanol (1) + propylamine (2) at 298.15 K: ○, P = 1.01 bar; □, P = 244.1 bar; △, P = 518.0 bar; —, eq 4.

though their molecular sizes are not remarkably different. Alkanol molecules self-associate strongly (OH···OH interaction) while the amine molecules self-associate rather marginally (*8*), and this has a dramatic influence on the thermophysical properties studied. The above holds true when comparing butylamine with the same alkanols (*4*).

In Figures 1–4, all binary systems studied exhibit relatively large negative excess volumes which persist over the pressure range studied here. V^E is especially large (negative) in the mixture with methanol and decreases as the chain length of the alkanol increases. The largest negative enthalpies of mixing measured at 25 °C are −3728, −2910, −2881, and −2674 J/mol for the mixtures of propylamine with methanol, ethanol, 1-propanol, and 1-butanol, respectively (*3*). The trends in these values are similar to those of the excess volumes and indicate that the hydrogen bonding of propylamine with the methanol molecule is much stronger than with the other lower alkanols. The relatively large negative excess volume of propylamine + methanol is indicative of a most efficient packing of the molecules in the mixture.

As observed, however, in Figures 5–8, the strength of the intermolecular hydrogen bonding is not the only factor influencing the viscosity deviation of liquid mixtures. The molecular sizes and shapes of the components are equally (if not more) important factors. It is doubtless however that the strength of hydrogen bonding between the methanol and propylamine molecules is the main factor for the

Table 11. Coefficients h_j of Eq 4 and Percent Absolute Average Deviation (% AAD)

	P = 1.013 bar	P = 244.1 bar	P = 518.0 bar
	Methanol (1) + Propylamine (2)		
h_0	0.5296	0.7599	1.0205
h_1	0.6658	0.7170	0.7760
h_2	0.0983	−0.0634	−0.2470
h_3	−0.3122	−0.1011	0.1393
h_4	−0.0298	−0.0077	0.0194
% AAD	0.2047	0.3991	0.6534
	Ethanol (1) + Propylamine (2)		
h_0	−0.2841	−0.2186	−0.1468
h_1	0.1163	0.1952	0.2168
h_2	0.0499	−0.0831	−0.2432
h_3	−0.0033	−0.1287	0.1559
h_4	−0.0042	0.1255	0.2840, −0.4997
% AAD	0.2055	5.7279	19.7058
	1-Propanol (1) + Propylamine (2)		
h_0	−1.2199	−1.2946	−1.3863
h_1	−0.4894	−0.4649	−0.4386
h_2	−0.4851	−0.8518	−1.2695
h_3	0.2079	0.1602	0.1057
h_4	0.3320	0.3698	0.4145
% AAD	1.4799	1.2955	1.6603
	1-Butanol (1) + Propylamine (2)		
h_0	−1.8392	−2.2118	−2.6454
h_1	−0.7619	−1.1640	−1.6222
h_2	−0.6783	−1.2180	−1.8348
h_3	0.0535	−0.0417	−0.1543
h_4	0.1134	0.0456	−0.0307
% AAD	0.3584	0.1055	0.0763

occurrence of the not too common positive viscosity deviation in their mixture. Figures 5−8 also show that, as the pressure increases, the viscosity deviation behaves much differently from the excess volumes. At least over the pressure range studied here, the viscosity deviation in the mixtures with methanol and ethanol increases as the pressure increases while in the other two mixtures the effect of pressure is the reverse. This behavior is similar to the behavior observed previously with the mixtures of butylamine with the same alkanols (*4*). This behavior is entirely different from the behavior in the other class of hydrogen-bonded systems studied in this laboratory, namely, the alkanol + alkane mixtures (*3*).

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