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Viscosity of Alkanol + Alkane Mixtures at Moderately High Pressures

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Measurements are reported for the dynamic viscosity of four binary alkanol + alkane mixtures of ethanol and 1-propanol with hexane and heptane. The measurements were conducted at 298.15 K and in a pressure range from atmospheric to 520 bar. A self-centering falling body viscometer was used for the measurements. All four systems exhibit negative viscosity deviations over the full composition and pressure ranges. The experimental data are discussed in terms of the specific interactions involved in the systems.

Introduction

In a recent publication (*1*) we have presented measurements on the dynamic viscosity of four alkanol + amine mixtures at moderately high pressures. In an effort to examine systematically the effect of hydrogen bonding on the basic thermophysical properties of mixtures, we present in this work the corresponding data for the dynamic viscosity of four binary alkanol + alkane mixtures. The key difference between the two classes of systems is that in alkanol + alkane mixtures the only type of hydrogen bonding involved is the self-association of alkanols while in the alkanol + amine mixtures besides self-association there is a strong propensity for cross-association of the type OH···NH between the alkanol and the amine. In other words, in the former systems the alkane is an inert solvent for the alkanol while in the latter the amine is an active solvent. It is expected that this difference in interactions will give rise to a significantly different behavior of the mixtures and, in particular, significantly different viscosity–composition behavior in the two classes of systems.

Experimental Section

All materials used were pro-analysis grades from Merck and were used as received. Their purity was verified by gas–liquid chromatography and was better than 99.5% for hexane, 99% for heptane, 99.8% for ethanol, and 99.5% for 1-propanol. Pure component properties are given 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.

The liquid densities, ρ, were measured with two vibrating tube densitometers, models 60/602 (atmospheric pressure) and 60/512 (high pressure) of Anton Paar. The estimated error in the density at atmospheric pressure is $\pm 5 \times 10^{-6}$ g·cm^{-3} while the corresponding error in the density at higher pressure is $\pm 1 \times 10^{-4}$ g·cm^{-3}. The density data for our systems at moderate pressures have been presented earlier (*2, 3*).

For the measurement of the dynamic 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 used, its operating principle, and the working equations have been fully described previously (*1*). 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 (*1*).

Table 1. Properties of Pure Components at 1.013 bar

liquid	t/°C	ρ/(kg·m^{-3}) measd	ρ/(kg·m^{-3}) lit.	η/(mPa·s) measd	η/(mPa·s) lit.
ethanol	25	785.19	785.12 (*5*)	1.0870	1.087 (*6*)
1-propanol	25	799.63	799.69 (*5*)	1.9680	1.968 (*6*)
hexane	25	654.90	654.80 (*7*)	0.2964	0.2964 (*8*)
heptane	25	679.42	679.57 (*5*)	0.3912	0.3905 (*8*)

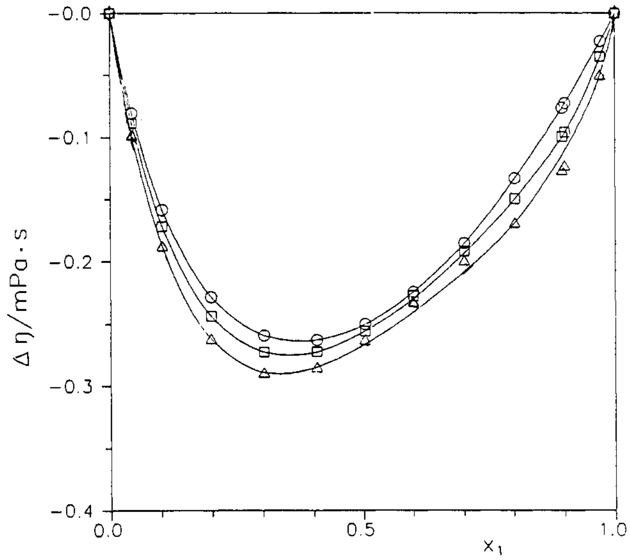

Figure 1. Viscosity deviation for the system hexane (1) + ethanol (2) at 298.15 K: ○, P = 1.01 bar; □, P = 2.44.1 bar; △, P = 518.0 bar; —, eq 2.

Results

For each binary system we have conducted viscosity measurements at at least ten intermediate compositions (plus two for the pure components) and at various pressures from atmospheric to 520 bar, for each composition. In Tables 2–5 are reported the experimental dynamic viscosities for the four studied systems. From these data on viscosities one can calculate the viscosity deviation, $\Delta\eta$, of the mixture defined by

$$\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2 \qquad (1)$$

In Figures 1–4 are shown the experimental viscosity deviations of the four binary mixtures at four external pressures. The

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

	η/(mPa·s)												
P/bar	$x_1 =$ 0.0000	$x_1 =$ 0.0432	$x_1 =$ 0.1024	$x_1 =$ 0.1981	$x_1 =$ 0.3027	$x_1 =$ 0.4066	$x_1 =$ 0.5031	$x_1 =$ 0.5999	$x_1 =$ 0.7007	$x_1 =$ 0.8026	$x_1 =$ 0.8955	$x_1 =$ 0.9710	$x_1 =$ 1.0000
1.0	1.0870	0.9721	0.8480	0.7020	0.5885	0.5026	0.4390	0.3881	0.3479	0.3191	0.3025	0.2965	0.2964
44.7	1.1188	1.0015	0.8753	0.7271	0.6118	0.5245	0.4598	0.4073	0.3644	0.3319	0.3122	0.3065	0.3081
94.6	1.1551	1.0352	0.9066	0.7558	0.6384	0.5496	0.4834	0.4293	0.3834	0.3465	0.3232	0.3180	0.3215
144.4	1.1915	1.0690	0.9380	0.7845	0.6651	0.5747	0.5072	0.4513	0.4024	0.3611	0.3343	0.3295	0.3350
194.3	1.2281	1.1030	0.9694	0.8134	0.6919	0.5998	0.5309	0.4734	0.4214	0.3758	0.3454	0.6410	0.3484
244.1	1.2647	1.1370	1.0009	0.8423	0.7187	0.6250	0.5548	0.4955	0.4405	0.3905	0.3565	0.3525	0.3619
294.0	1.3015	1.1711	1.0325	0.8712	0.7455	0.6502	0.5787	0.5176	0.4597	0.4053	0.3676	0.3641	0.3755
343.8	1.3384	1.2053	1.0642	0.9002	0.7724	0.6755	0.6026	0.5398	0.4789	0.4200	0.3787	0.3757	0.3890
393.6	1.3754	1.2396	1.0960	0.9293	0.7994	0.7008	0.6265	0.5620	0.4981	0.4348	0.3899	0.3873	0.4026
443.5	1.4125	1.2740	1.1278	0.9585	0.8264	0.7261	0.6505	0.5842	0.5174	0.4497	0.4011	0.3990	0.4163
493.4	1.4498	1.3085	1.1598	0.9877	0.8534	0.7514	0.6745	0.6064	0.5367	0.4645	0.4123	0.4107	0.4300
518.0	1.4683	1.3256	1.1756	1.0022	0.8668	0.7640	0.6864	0.6175	0.5463	0.4719	0.4179	0.4165	0.4368

Table 3. Experimental Viscosities for the System Hexane (1) + 1-Propanol (2) at 298.15 K

	η/(mPa·s)											
P/bar	$x_1 =$ 0.0000	$x_1 =$ 0.0603	$x_1 =$ 0.0992	$x_1 =$ 0.2086	$x_1 =$ 0.3018	$x_1 =$ 0.4056	$x_1 =$ 0.5016	$x_1 =$ 0.5979	$x_1 =$ 0.7014	$x_1 =$ 0.8029	$x_1 =$ 0.9039	$x_1 =$ 0.9486
1.0	1.9680	1.6192	1.4402	1.0697	0.824	0.6737	0.5493	0.4564	0.3861	0.3407	0.3116	0.3029
44.7	2.0395	1.6694	1.4828	1.1043	0.8861	0.7048	0.5753	0.4756	0.3989	0.3504	0.3220	0.3141
94.6	2.1212	1.7269	1.5315	1.1440	0.9246	0.7405	0.6050	0.4975	0.4135	0.3615	0.3338	0.3269
144.4	2.2031	1.7845	1.5803	1.1838	0.9632	0.7762	0.6348	0.5194	0.4281	0.3726	0.3457	0.3397
194.3	2.2854	1.8424	1.6293	1.2237	1.0019	0.8120	0.6645	0.5414	0.4427	0.3838	0.3576	0.3525
244.1	2.3679	1.9004	1.6784	1.2637	1.0406	0.8479	0.6944	0.5634	0.4574	0.3951	0.3695	0.3654
294.0	2.4507	1.9585	1.7276	1.3038	1.0795	0.8838	0.7242	0.5855	0.4721	0.4064	0.3815	0.3783
343.8	2.5338	2.0169	1.7771	1.3441	1.1184	0.9198	0.7542	0.6076	0.4869	0.4177	0.3935	0.3913
393.6	2.6171	2.0754	1.8266	1.3844	1.1575	0.9559	0.7842	0.6297	0.5017	0.4291	0.4056	0.4042
443.5	2.7007	2.1341	1.8764	1.4249	1.1966	0.9920	0.8142	0.6519	0.5165	0.4405	0.4176	0.4172
493.4	2.7846	2.1930	1.9262	1.4655	1.2359	1.0282	0.8443	0.6742	0.5315	0.4520	0.4298	0.4303
518.0	2.8263	2.2222	1.9510	1.4857	1.2554	1.0462	0.8593	0.6852	0.5389	0.4577	0.4358	0.4367

Table 4. Experimental Viscosities for the System Heptane (1) + Ethanol (2) at 298.15 K

	η/(mPa·s)												
P/bar	$x_1 =$ 0.0000	$x_1 =$ 0.0472	$x_1 =$ 0.1004	$x_1 =$ 0.1990	$x_1 =$ 0.3003	$x_1 =$ 0.3994	$x_1 =$ 0.5070	$x_1 =$ 0.5988	$x_1 =$ 0.6751	$x_1 =$ 0.7394	$x_1 =$ 0.8085	$x_1 =$ 0.9003	$x_1 =$ 1.0000
1.0	1.0870	1.0018	0.9149	0.7776	0.6663	0.5825	0.5154	0.4742	0.4490	0.4327	0.4191	0.4048	0.3912
20.0	1.1008	1.0154	0.9287	0.7900	0.6791	0.5940	0.5256	0.4835	0.4580	0.4416	0.4279	0.4136	0.3991
119.7	1.1734	1.0866	1.0010	0.8550	0.7462	0.6546	0.5798	0.5323	0.5053	0.4886	0.4741	0.4598	0.4410
219.4	1.2466	1.1583	1.0736	0.9203	0.8136	0.7155	0.6341	0.5813	0.5528	0.5357	0.5204	0.5062	0.4830
319.1	1.3201	1.2305	1.1467	0.9859	0.8812	0.7765	0.6887	0.6305	0.6004	0.5830	0.5669	0.5527	0.5251
418.8	1.3942	1.3030	1.2201	1.0519	0.9491	0.8378	0.7434	0.6798	0.6481	0.6304	0.6135	0.5994	0.5674
518.5	1.4687	1.3760	1.2939	1.1182	1.0174	0.8992	0.7983	0.7293	0.6961	0.6780	0.6603	0.6462	0.6098

Table 5. Experimental Viscosities for the System Heptane (1) + 1-Propanol (2) at 298.15 K

	η/(mPa·s)												
P/bar	$x_1 =$ 0.0000	$x_1 =$ 0.0569	$x_1 =$ 0.1025	$x_1 =$ 0.1996	$x_1 =$ 0.3052	$x_1 =$ 0.4045	$x_1 =$ 0.5038	$x_1 =$ 0.6039	$x_1 =$ 0.7066	$x_1 =$ 0.8001	$x_1 =$ 0.8488	$x_1 =$ 0.9551	$x_1 =$ 1.0000
1.0	1.9680	1.6541	1.4527	1.1383	0.9086	0.7500	0.6265	0.5366	0.4713	0.4307	0.4168	0.4008	0.3912
44.7	2.0395	1.7140	1.5056	1.1828	0.9489	0.7853	0.6569	0.5642	0.4963	0.4511	0.4354	0.4188	0.4096
94.6	2.1212	1.7826	1.5662	1.2338	0.9948	0.8257	0.6917	0.959	0.5249	0.4746	0.4567	0.4394	0.4304
144.4	2.2031	1.8514	1.6269	1.2848	1.0409	0.8663	0.7265	0.6276	0.5535	0.4981	0.4780	0.4601	0.4513
194.3	2.2854	1.9205	1.6878	1.3361	1.0870	0.9069	0.7614	0.6593	0.5821	0.5216	0.4994	0.4809	0.4722
244.1	2.3679	1.9897	1.7488	1.3875	1.1333	0.9476	0.7962	0.6912	0.6108	0.5453	0.5209	0.5017	0.4933
294.0	2.4507	2.0592	1.8100	1.4390	1.1796	0.9885	0.8312	0.7231	0.6395	0.5690	0.5424	0.5226	0.5144
343.8	2.5338	2.1289	1.8714	1.4907	1.2260	1.0294	0.8662	0.7551	0.6683	0.5928	0.5639	0.5436	0.5355
393.6	2.6171	2.1988	1.9330	1.5426	1.2726	1.0705	0.9013	0.7872	0.6971	0.6166	0.5855	0.5647	0.5567
443.5	2.7007	2.2689	1.9948	1.5946	1.3193	1.1116	0.9365	0.8193	0.7260	0.6406	0.6072	0.5859	0.5780
493.4	2.7846	2.3393	2.0568	1.6467	1.3661	1.1529	0.9718	0.8516	0.7550	0.6646	0.6290	0.6071	0.5994
518.0	2.8263	2.3742	2.0876	1.6726	1.3894	1.1734	0.9893	0.8676	0.7694	0.6765	0.6398	0.6176	0.6100

solid line in these figures were calculated by fitting to the experimental data the Redlich–Kister-type equation

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

Coefficients h_j along with the standarad deviation of fit (% AAD = $100[\sum_{i=1}^{N}|(\Delta\eta_{i,\,\mathrm{exp}} - \Delta\eta_{i,\,\mathrm{calc}})/\Delta\eta_{i,\,\mathrm{exp}}|/N]$, N being the number of experimental data) are reported in Table 6.

As already mentioned the densities have been measured over a pressure range up to ca. 400 bar (*2*, *3*). The densities above 400 bar have been calculated with a procedure described earlier (*1*). From the densities one can calculate the excess volumes, V^{E}, of the mixtures defined by

$$V^{\mathrm{E}} = V - x_1V_1 - x_2V_2 = x_1M_1\left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + x_2M_2\left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \qquad (3)$$

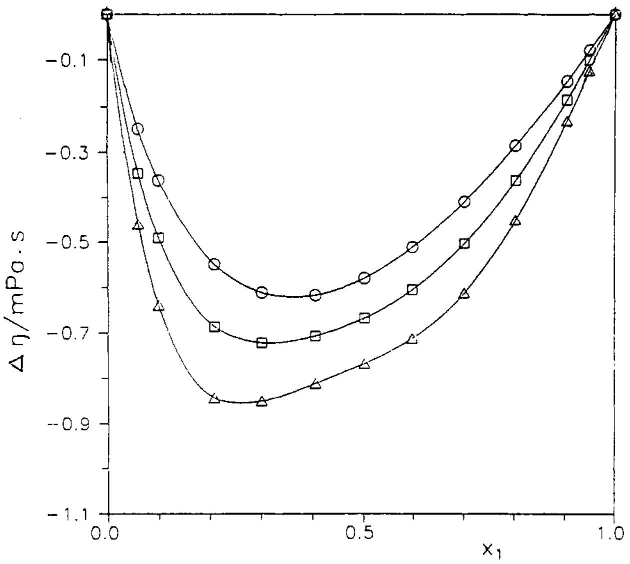

Figure 2. Viscosity deviation for the system hexane (1) + 1-propanol (2) at 298.15 K: ○, P = 1.01 bar; □, P = 244.1 bar; △, P = 518.0 bar; —, eq 2.

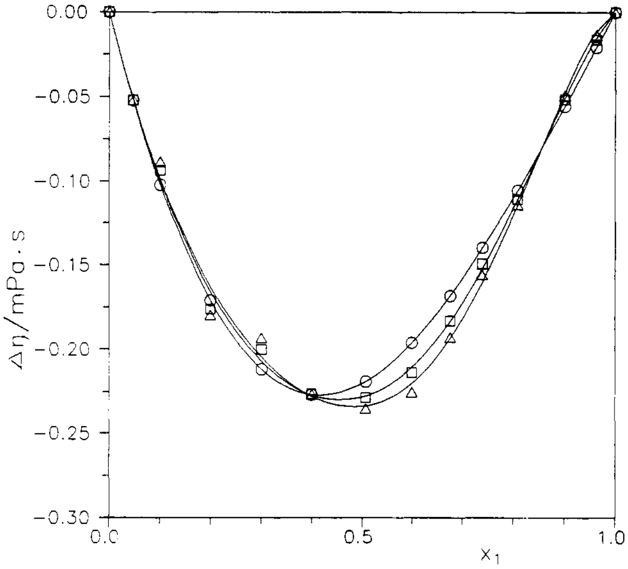

Figure 3. Viscosity deviation for the system heptane (1) + ethanol (2) at 298.15 K: ○, P = 1.01 bar; □, P = 2.44.1 bar; △, P = 518.0 bar; —, eq 2.

where V_j and M_j are the molar volume and mass, respectively, of component j. In direct analogy with eq 2 we may fit the V^E data to the equation

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1x_2\sum_{j=0}^{n} v_j(2x_1-1)^j \qquad (4)$$

For completeness we report in Table 7 the coefficients v_j of eq 4 for three representative pressures.

Discussion

As shown in Table 1 the two alkanols have much higher viscositites than the two alkanes although the latter have longer chain lengths. The self-association of alkanols seems to impart an effective chain length which is much longer than the corresponding molecular length. On the other hand the isothermal compressibility of hexane, heptane, ethanol, and 1-propanol at 298.15 K is equal to 1.515 × 10^{-4}, 1.349 × 10^{-4}, 1.079 × 10^{-4}, and 0.942 × 10^{-4} bar^{-1}, respectively (*2–4*). The emerging picture is clear: the larger the effective chain length the lower the isothermal compressibility.

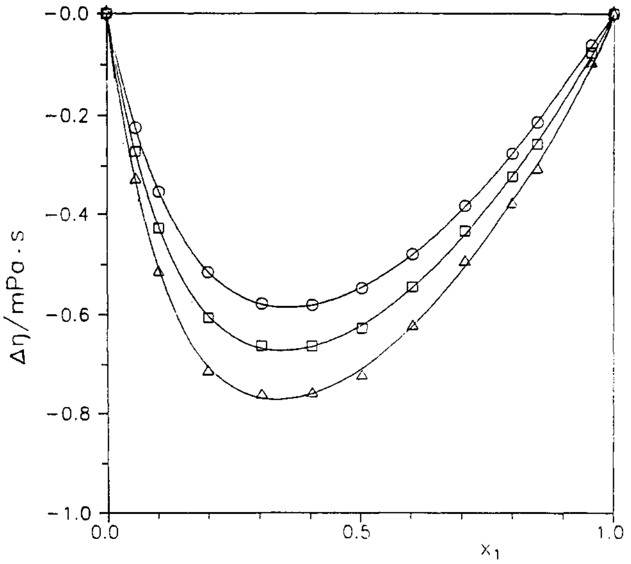

Figure 4. Viscosity deviation for the system heptane (1) + 1-propanol (2) at 298.15 K: ○, P = 1.01 bar; □, P = 244.1 bar; △, P = 518.0 bar; —, eq 2.

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

	P = 1.013 bar	P = 244.1 bar	P = 518.0 bar
	Hexane (1) + Ethanol (2)		
h_0	-1.0036	-1.0259	-1.0554
h_1	0.3918	0.4734	0.5700
h_2	-0.3126	-0.4281	-0.5540
h_3	0.2786	0.0412	-0.2324
h_4	-0.1676	-0.4283	-0.7342
% AAD	0.0369	0.0231	0.0115
	Hexane (1) + 1-Propanol (2)		
h_0	-2.3243	-2.6724	-3.0766
h_1	1.0909	1.0234	0.9523
h_2	-0.6198	-1.4849	-2.4520
h_3	0.6048	1.6600	2.8647
h_4	-0.3430	-0.4527	-0.6070
% AAD	0.0116	0.0099	0.0055
	Heptane (1) + 1-Propanol (2)		
h_0	-2.1875	-2.4908	-2.8420
h_1	1.0042	1.1729	1.3643
h_2	-0.7321	-0.9239	-1.1470
h_3	0.6723	0.8312	1.0269
h_4	-0.1296	-0.4834	-0.8740
% AAD	0.4342	1.2517	1.9264
	Heptane (1) + Ethanol (2)		
h_0	-0.8800	-0.9121	-0.9347
h_1	0.3227	0.1650	0.0667
h_2	0.0027	0.0391	0.0639
h_3	-0.0055	0.2667	0.4372
h_4	0.0039	0.1225	0.1954
% AAD	0.0271	2.1256	3.6241

As is shown in Figures 1–4 in all four studied systems the visocsity deviation, Δη, is negative over the full composition range. For a given alkanol, the effect on Δη of the two n-alkanes is not significantly different compared to the corresponding effect of the two alkanols for a given n-alkane. One could explain the more negative viscosity difference, Δη, in the mixtures of 1-propanol on the basis of the breaking by n-alkanes of a more dense and more ordered structure compared to the structure in ethanol mixtures. The extreme values of the heats of mixing in all four systems are comparable, ranging from 586 to 646 J·mol^{-3}. This implies that the above-mentioned differences in Δη are not due to

Table 7. Coefficients v_j of Eq 4 and Percent Average Absolute Deviation of Fit (% AAD)

	P = 1.013 bar	P = 198.9 bar	P = 338.1 bar
	Hexane (1) + Ethanol (2)		
v_0	1.5655	1.2926	1.2210
v_1	0.2133	0.0494	−0.0379
v_2	0.6192	0.7133	0.5788
v_3	0.7714	0.6976	0.7183
v_4	0.7389	0.3125	0.4650
% AAD	4.9219	4.7340	4.8958
	Hexane (1) + 1-Propanol (2)		
v_0	0.6320	0.6402	0.6073
v_1	0.7433	0.5522	0.4825
v_2	0.2850	0.2024	0.0613
v_3	0.6989	0.5941	0.5399
v_4	0.6966	0.8564	0.9623
% AAD	4.1676	3.1940	3.1450
	Heptane (1) + Ethanol (2)		
v_0	1.8657	1.5811	1.3801
v_1	0.0223	−0.1310	−0.2068
v_2	0.3632	0.2976	0.3056
v_3	0.6920	0.9400	0.8466
v_4	1.0749	1.1154	0.7358
% AAD	1.5474	4.5692	5.1168
	Heptane (1) + 1-Propanol (2)		
v_0	1.1464	1.0154	0.9401
v_1	0.6280	0.4689	0.3840
v_2	0.6137	0.6771	0.2603
v33	0.5741	0.5285	0.4778
v_4			0.8108
% AAD	4.3911	2.8775	2.6935

the different extents of hydrogen bond breakage in the ethanol and 1-propanol systems but rather to the different chain lengths of the two alkanols.

It is worth contrasting the $\Delta\eta$ vs composition profiles of this work with the corresponding profiles of the mixtures of the two alkanols with n-butylamine published previously (*1*). In the ethanol + n-butylamine system $\Delta\eta$ is positive at the higher pressures and s-shaped at the lower pressures. In the 1-propanol + n-butylamine mixture $\Delta\eta$ is negative but less so compared to the 1-propanol + alkane mixtures of the present work, the extreme value for the former system being −0.254 mPa·s (*1*, *4*). This difference, certainly, arises from the presence of the strong cross-association of the type OH···NH in the alkanol + amine systems which is absent in the alkanol + alkane systems of this work.

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