Viscosities and Densities of Hexane + Butan-1-ol, + Hexan-1-ol, and + Octan-1-ol at 298.15 K

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Viscosities and densities have been measured for hexane + butan-1-ol, + hexan-1-ol, and + octan-1-ol at 298.15 K and atmospheric pressure. Kinematic viscosities was determined using a capillary viscosimeter, and densities were measured by vibrating-tube densimetry. The viscosity deviations were evaluated. Viscosity results were fitted to the equations of Grunberg-Nissan, McAllister, Auslander, and Teja.

Introduction

In continuation of our studies on the thermodynamic and transport properties of (alkan-1-ols + n-alkanes) (*1–3*), we report measurements of viscosities of hexane + butan-1-ol, + hexan-1-ol, and + octan-1-ol at 298.15 K and atmospheric pressure. Kinematic viscosities were determined using a capillary viscosimeter, and densities were measured by a vibrating-tube densimeter.

The results were used to calculate the viscosity deviations and excess molar volumes. The viscosities were used to test the semiempirical relations of Grunberg-Nissan (*4*), McAllister (*5, 6*), Auslander (*7*), and Teja (*8, 9*).

Experimental Section

The following Fluka chemicals were used: hexane (x > 0.995), butan-1-ol (x > 0.995), hexan-1-ol (x > 0.995), and octan-1-ol (x > 0.995). The substances were degassed and dried over molecular sieves (Union Carbide, type 0.4 nm). The measured densities and viscosities of the pure component liquids are listed in Table 1 together with literature values.

Densities of the pure components and their mixtures were measured with an Anton Paar Model DMA 60/602 densimeter with a resolution of ±2 × 10^{-6} g·cm^{-3} and kinematic viscosities by the automatic Schott-Geräte measuring system with a resolution of ±5 × 10^{-4} mm^2·s^{-1}. The temperature was regulated to better than 0.01 K. The experimental techniques have been described previously (*16, 17*). Mixtures were prepared by mass using a Mettler AT201; the precision of the mole fractions is estimated to better than ±1 × 10^{-4}.

Results and Discussion

Densities and viscosities are listed in Table 2. The viscosity deviation was calculated by

$$\Delta\eta = \eta - \{x_1\eta_1 + x_2\eta_2\} \tag{1}$$

Table 1. Data for Pure Liquids at the Temperature 298.15 K

	ϱ/(g·cm^{-3})		η/(mPa·s)	
liquid	exptl	lit.	exptl	lit.
hexane	0.655 05	0.655 03 (*10*)	0.2861	0.2968 (*13*)
butan-1-ol	0.805 81	0.805 80 (*1*)	2.550	2.571 (*13*)
hexan-1-ol	0.815 32	0.815 15 (*11*)	4.862	4.317 (*14*)
octan-1-ol	0.821 62	0.821 61 (*12*)	7.596	7.363 (*15*)

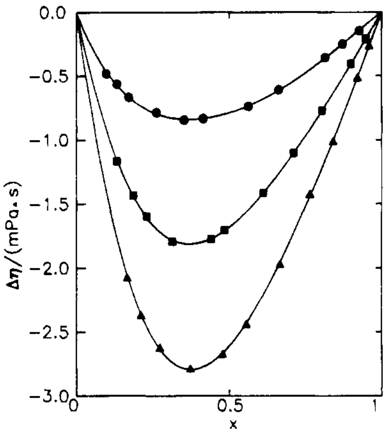

Figure 1. Experimental $\Delta\eta$ at 298.15 K of x $CH_3(CH_2)_4CH_3$ + (1 − x) $CH_3(CH_2)_nOH$: ○, n = 3; ■, n = 5; △, n = 7. The curves have been calculated from eq 2.

The experimental values of $\Delta\eta$ and V^E, at 298.15 K, are also reported in Table 2. Excess volumes and viscosity deviations were fitted to

$$Q = x_1 x_2 \sum_{i=0}^{m} A_i (x_1 - x_2)^i \tag{2}$$

where $Q = \Delta\eta$/(mPa·s) or $Q = V^E$/(cm^3·mol^{-1}). The parameters A_i and the corresponding standard deviations σ given in Table 3 were calculated using the unweighted least-squares method, with the degree of the polynomial previously optimized through the application of the F-test (*18*).

The differences between the experimental excess molar volumes of the literature (*1–19*) and our results fitted with eq 2 were about 0.007 cm^3·mol^{-1} for hexane + butan-1-ol, 0.02 cm^3·mol^{-1} for hexane + hexan-1-ol, and 0.04 cm^3·mol^{-1} for hexane + octan-1-ol.

Figures 1 and 2 show the experimental $\Delta\eta$ and V^E plotted against x together with the fitted curve. The $\Delta\eta$ is negative and decreases with increasing carbon number of the alkan-1-ol. The V^E increases with the carbon number of the 1-alkanol with values close to zero for the hexane + butan-1-ol and negative for hexane + hexan-1-ol and octan-1-ol.

The results obtained for excess magnitudes are compared in Table 4 with other magnitudes of the same mixtures,

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Table 2. Densities, Viscosities, Excess Molar Volumes, and Viscosity Deviation at 298.15 K

x	ϱ/(g·cm^{-3})	η/(mPa·s)	V^E/(cm^3·mol^{-1})	$\Delta\eta \times 10^3$/(mPa·s)
		x Hexane + (1 − x) Butan-1-ol		
0.0971	0.786 81	1.848	−0.1345	−0.482
0.1322	0.780 14	1.688	−0.1636	−0.563
0.1707	0.772 97	1.496	−0.1839	−0.667
0.2625	0.756 42	1.169	−0.1990	−0.787
0.3521	0.741 08	0.909	−0.1707	−0.845
0.4142	0.730 91	0.778	−0.1330	−0.834
0.5620	0.708 39	0.539	−0.0265	−0.739
0.6624	0.694 38	0.440	0.0467	−0.610
0.8147	0.675 24	0.348	0.0906	−0.357
0.8728	0.668 56	0.323	0.0807	−0.251
0.9267	0.662 72	0.306	0.0448	−0.146
		x Hexane + (1 − x) Hexan-1-ol		
0.1327	0.794 24	3.088	−0.1760	−1.166
0.1854	0.785 77	2.578	−0.2173	−1.435
0.2308	0.778 45	2.207	−0.2462	−1.599
0.3137	0.765 00	1.632	−0.2756	−1.794
0.4404	0.744 43	1.072	−0.2768	−1.775
0.4841	0.737 32	0.941	−0.2657	−1.706
0.6117	0.716 59	0.648	−0.2057	−1.415
0.7122	0.700 31	0.501	−0.1312	−1.102
0.8046	0.685 48	0.408	−0.0614	−0.772
0.8997	0.670 48	0.338	−0.0075	−0.407
0.9493	0.662 79	0.309	0.0044	−0.209
		x Hexane + (1 − x) Octan-1-ol		
0.1657	0.799 45	4.313	−0.2695	−2.072
0.2119	0.792 89	3.677	−0.3191	−2.370
0.2740	0.783 90	2.968	−0.3869	−2.625
0.3717	0.769 17	2.093	−0.4656	−2.786
0.4775	0.752 31	1.432	−0.4925	−2.673
0.5556	0.739 20	1.096	−0.4677	−2.438
0.6659	0.719 87	0.759	−0.4049	−1.969
0.7638	0.701 84	0.559	−0.3096	−1.453
0.8406	0.687 18	0.443	−0.2292	−1.008
0.9211	0.671 27	0.350	−0.1244	−0.513
0.9597	0.663 56	0.319	−0.0965	−0.262

Table 3. Parameters A_i of Eq 2 and Standard Deviations σ

	A_0	A_1	A_2	A_3	σ
		x Hexane + (1 − x) Butan-1-ol			
V^E	−0.2245	1.5887			0.002
$\Delta\eta$	−3.151	1.439	−0.887	0.793	0.010
		x Hexane + (1 − x) Hexan-1-ol			
V^E	−1.0411	0.7296	0.3402	0.3189	0.001
$\Delta\eta$	−6.733	3.708	−1.166		0.006
		x Hexane + (1 − x) Octan-1-ol			
V^E	−1.8738	0.2846	0.3982		0.007
$\Delta\eta$	−10.440	5.506	−1.704		0.006

and show agreement with the trends found in previous work (*1–3*). In these mixtures the behavior of V^E is contrary to the $\Delta\epsilon'$. This is due to the fact that when V^E decreases, the number of dipoles per volume unit increases. The $\Delta\epsilon''$ shows behavior opposite of that of the $\Delta\eta$, H^E, and G^E due to weaker interactions in the mixture. The excess molar volumes and viscosity increments decrease as the length of the 1-alcohol chain increases.

Semiempirical Relations

Several semiempirical relations have been proposed to estimate dynamic viscosity (η). Grunberg-Nissan (*4*) suggested the expression

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_w \tag{3}$$

where x_1 is the mole fraction of hexane and x_2 that of the alkan-1-ol, η_1 and η_2 are the dynamic viscosities of hexane and alkan-1-ol, and d_w is a parameter proportional to the interchange energy.

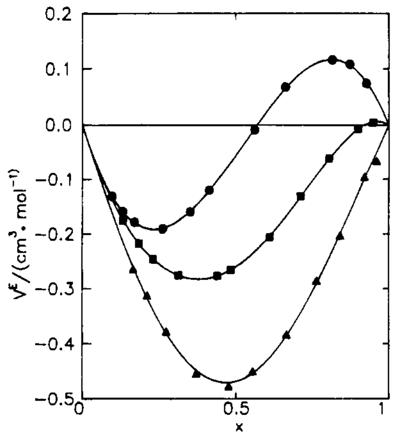

Figure 2. Experimental ΔG^* at 298.15 K of x $CH_3(CH_2)_4CH_3$ + (1 − x) $CH_3(CH_2)_nOH$: ○, n = 3; ■, n = 5; △, n = 7. The curves have been calculated from eq 2.

Table 4. Excess Molar Volumes, Viscosity Deviations, Excess Molar Enthalpies, Dielectric-Permittivity Increments, and Excess Molar Gibbs Energies at 298.15 K

V^E	$\Delta\eta$/ (mPa·s)	H^E/ (J·mol^{-1})	$\Delta\epsilon'$	$\Delta\epsilon''$	G^E/ (J·mol^{-1})
		0.5 Hexane + 0.5 Butan-1-ol			
−0.0561	−0.7877	515 (*20*)	−0.276 (1)	−0.930 (*1*)	1140 (*21*)
		0.5 Hexane + 0.5 Hexan-1-ol			
−0.2602	−1.6833	505 (*22*)	0.111 (*1*)	−0.276 (*1*)	975 (*23*)
		0.5 Hexane + 0.5 Octan-1-ol			
−0.4684	−2.6100	456 (*24*)	0.180 (*1*)	−0.057 (*1*)	

Table 5. Parameters of Eqs 3–5 and 11 and Standard Deviations σ

eq				σ
		x Hexane + (1 − x) Butan-1-ol		
3	$d_w = -1.1455$			0.013
4	$\eta_{12} = 0.3736$	$\eta_{21} = 0.8661$		0.010
5	$B_{12} = 1.4197$	$B_{21} = 0.1717$	$A_{21} = 0.3721$	0.008
11	$\alpha_{12} = 0.1241$			0.018
		x Hexane + (1 − x) Hexan-1-ol		
3	$d_w = -0.8588$			0.040
4	$\eta_{12} = 0.4224$	$\eta_{21} = 1.5874$		0.009
5	$B_{12} = 0.4666$	$B_{21} = 0.6339$	$A_{21} = 0.1379$	0.006
11	$\alpha_{12} = 0.2154$			0.024
		x Hexane + (1 − x) Octan-1-ol		
3	$d_w = -0.2480$			0.036
4	$\eta_{12} = 0.6647$	$\eta_{21} = 2.5444$		0.005
5	$B_{12} = 0.6131$	$B_{21} = 0.4947$	$A_{21} = 0.1809$	0.007
11	$\alpha_{12} = 0.6814$			0.027

The McAllister (*5*) equation was derived on the basis of the absolute reaction rate theory of Eyring (*6*):

$$\ln \eta = x_1^3 \ln \eta_1 + x_2^3 \ln \eta_2 + 3x_1^2 x_2 \ln \eta_{12} + 3x_1 x_2^2 \ln \eta_{21} - \ln\{x_1 + x_2 M_2/M_1\} + 3x_1^2 x_2 \ln\{2/3 + M_2/3M_1\} + 3x_1 x_2^2 \ln(1/3 + 2M_2/3M_1) + x_2^3 \ln(M_2/M_1) \tag{4}$$

where η_{12} and η_{21} are the interaction parameters and M is the molar mass.

The Auslander (*7*) equation, the less complex three-parameter equation, has the following form:

$$x_1\{x_1 + B_{12}x_2(\eta - \eta_1)\} + A_{21}x_2\{B_{21}x_1 + x_2(\eta - \eta_2)\} = 0 \tag{5}$$

here B_{12}, A_{21}, and B_{21} are the parameters representing binary interactions.

On the basis of the corresponding states treatment for mixture compressibility factors (*25*, *26*), Teja and Rice (*8*, *9*) proposed the following expression for liquid mixture viscosity:

$$\ln(\eta\xi) = x_1 \ln(\eta_1\xi_1) + x_2 \ln(\eta_2\xi_2) \qquad (6)$$

where $\xi = V_c^{2/3}/(T_cM)^{1/2}$ and V_c and T_c are the critical temperature and critical volume, respectively. The values of the mixture at each composition were evaluated by using

$$V_c = x_1^2V_{c1} + x_2^2V_{c2} + 2x_1x_2V_{c12} \qquad (7)$$

$$T_c = \{x_1^2T_{c1}V_{c1} + x_2^2T_{c2}V_{c2} + 2x_1x_2T_{c12}V_{c12}\}/V_c \qquad (8)$$

$$M = x_1M_1 + x_2M_2 \qquad (9)$$

$$V_{c12} = \{(V_{c1}^{1/3} + V_{c2}^{1/3})/2\}^3 \qquad (10)$$

$$T_{c12}V_{c12} = \alpha_{12}(T_{c1}V_{c1}T_{c2}V_{c2})^{1/2} \qquad (11)$$

where α_{12} is an "empirical" interaction parameter.

Table 5 gives the parameters calculated and the standard deviations between experimental values obtained using the eqs 3–5 and 11. The values of T_c and V_c used in eq 11 for pure components were obtained from ref 15.

Registry Numbers Supplied by Author. hexane, 110-54-3; butan-1-ol, 71-36-3; hexan-1-ol, 111-27-3; octan-1-ol, 111-87-5.

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