

Viscosities and Densities for Binary Mixtures of Benzylamine with 1-Pentanol, 2-Pentanol, 2-Methyl-1-butanol, 2-Methyl-2-butanol, 3-Methyl-1-butanol, and 3-Methyl-2-butanol

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Viscosities and densities were measured for the binary mixtures of benzylamine with 1-pentanol, 2-pentanol, 2-methyl-1-butanol, 2-methyl-2-butanol, 3-methyl-1-butanol, and 3-methyl-2-butanol at temperatures from 298.15 K to 308.15 K. A pycnometer and Cannon–Fenske routine viscometer were used to determine density and kinematic viscosity, respectively. The calculated excess molar volumes V^E and viscosity deviations $\delta\eta$ for each binary system were found to be negative over the whole range of mixture compositions. Redlich–Kister type equations were fitted to the isothermal excess molar volumes and viscosity deviations, and the kinematic viscosity data were correlated with the McAllister equation.

Introduction

To investigate the effects of the molecular structure of alcohol isomers on excess molar volumes and viscosity deviations, a series of density and viscosity measurements were conducted in our laboratory. This paper reports the results of the binary systems composed of benzylamine and six C_5 -alcohol isomers at temperatures from 298.15 K to 308.15 K. No available data were found in the literature for these binary mixtures at the experimental conditions of this study.

Experimental Section

Benzylamine (99%), 1-pentanol (99%), 2-pentanol (98%), and 2-methyl-2-butanol (99%) were Riedel–de Haën products, and 2-methyl-1-butanol (98%), 3-methyl-1-butanol (99%), and 3-methyl-2-butanol (99%) were supplied by Fluka Chemie AG. The purities of these substances were checked with gas chromatography. All chemicals were used without further purification. The measured densities and viscosities for these pure substances at 303.15 K were compared with literature values in Table 1.

The densities were determined with a pycnometer having a nominal internal volume of 25 cm³. The internal volume of the pycnometer was calibrated with pure water (Riddick and Bunger, 1986) at each temperature of interest. The sample mixture was prepared by mass with an accuracy of ± 0.0001 in mole fraction. To minimize the evaporation during the sample preparation, the heavier component was charged first. Three loaded pycnometers were immersed in a thermostatic bath (Neslab GP-500), which was controlled to within ± 0.03 K. A precision digital thermometer (model 1560, Hart Scientific) with a thermistor probe was used to read the temperature with an accuracy of ± 0.015 K. The mixture densities were obtained by averaging the results from these three pycnometers. The uncertainty of reported densities was estimated to be less than $\pm 0.1\%$. Frequent checks of mixture composition by gas chroma-

Table 1. Viscosities η and Densities ρ of Pure Components at 303.15 K

compound	$\eta/\text{mPa}\cdot\text{s}$		$\rho/\text{g}\cdot\text{cm}^{-3}$	
	exptl	lit.	exptl	lit.
benzylamine	1.492	1.50 ^a	0.9732	0.9737 ^a
1-pentanol	3.056	3.054 ^b 3.00 ^f	0.8072	0.8079 ^b 0.8076 ^e 0.8073 ^f 0.80694 ^g
2-pentanol	2.882	2.884 ^b 2.77 ^f	0.8013	0.8013 ^b 0.8010 ^f
2-methyl-1-butanol	3.594	3.5956 ^b	0.8110	0.8109 ^b
2-methyl-2-butanol	2.857	2.856 ^b 2.87 ^f	0.8001	0.8000 ^b 0.8006 ^f
3-methyl-1-butanol	3.194	3.195 ^b 2.961 ^d 2.95 ^f	0.8017	0.8037 ^b 0.80178 ^c 0.80174 ^d 0.8027 ^f
3-methyl-2-butanol	3.161	3.163 ^b	0.8094	0.8093 ^b

^a Lee et al. (1993). ^b TRC data (1994). ^c Kumar et al. (1992). ^d Venkatesulu et al. (1996). ^e Vijayalakshmi and Naidu (1990). ^f Riggio et al. (1986). ^g Choudary and Kudchadker (1992).

tography showed that its variation was minimal even after the measurements were completed.

The kinematic viscosities ν were measured by using Cannon–Fenske routine viscometers (size 75, supplied by Cannon Instrument Co.). The viscometer had been calibrated with twice-distilled water over the entire range of experimental conditions. The detailed procedure of viscosity measurements was presented elsewhere (Weng, 1999). The kinematic viscosities, ν (10^{-6} m²·s⁻¹) were obtained from the following equation:

$$\nu = kt \quad (1)$$

where k (10^{-6} m²·s⁻²) is the capillary constant of the viscometer and t (s) is the flowing time. The absolute viscosities η (mPa·s) were calculated from $\eta = \rho\nu$. The estimated uncertainty of the reported viscosities is $\pm 1.0\%$.

Results and Discussion

Experimental results for these six binary systems are listed in Tables 2–7. Figure 1 shows the variation of

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Table 2. Densities ρ and Viscosities η for Benzylamine (1) + 1-Pentanol (2)

x_1	$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K	
	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$
0.1000	0.8300	3.257	0.8261	2.820	0.8220	2.406
0.2004	0.8483	3.009	0.8443	2.607	0.8403	2.283
0.2999	0.8666	2.798	0.8625	2.436	0.8582	2.133
0.4000	0.8843	2.599	0.8801	2.250	0.8758	1.979
0.4997	0.9011	2.419	0.8967	2.124	0.8924	1.841
0.6000	0.9174	2.250	0.9132	1.971	0.9086	1.734
0.7003	0.9332	2.088	0.9288	1.842	0.9244	1.624
0.8000	0.9483	1.943	0.9441	1.720	0.9398	1.526
0.8999	0.9634	1.808	0.9589	1.616	0.9548	1.454

Table 3. Densities ρ and Viscosities η for Benzylamine (1) + 2-Pentanol (2)

x_1	$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K	
	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$
0.1000	0.8240	3.179	0.8197	2.626	0.8156	2.199
0.2002	0.8420	2.906	0.8378	2.395	0.8339	2.034
0.3001	0.8601	2.676	0.8560	2.192	0.8520	1.884
0.4001	0.8781	2.466	0.8740	2.038	0.8698	1.759
0.4997	0.8956	2.274	0.8914	1.893	0.8872	1.642
0.6000	0.9129	2.110	0.9084	1.765	0.9042	1.559
0.6989	0.9295	1.976	0.9251	1.666	0.9207	1.482
0.8000	0.9461	1.854	0.9417	1.587	0.9372	1.436
0.8998	0.9625	1.750	0.9580	1.532	0.9536	1.401

Table 4. Densities ρ and Viscosities η for Benzylamine (1) + 2-Methyl-1-butanol (2)

x_1	$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K	
	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$
0.1000	0.8330	4.232	0.8287	3.472	0.8245	2.453
0.2000	0.8508	3.772	0.8463	3.103	0.8424	2.227
0.3001	0.8683	3.382	0.8643	2.773	0.8603	2.020
0.3999	0.8852	3.039	0.8815	2.478	0.8774	1.837
0.5000	0.9018	2.708	0.8978	2.243	0.8938	1.711
0.6000	0.9180	2.435	0.9138	2.048	0.9097	1.595
0.6998	0.9335	2.181	0.9292	1.849	0.9250	1.500
0.7989	0.9490	1.984	0.9443	1.691	0.9397	1.423
0.8999	0.9643	1.796	0.9587	1.572	0.9549	1.377

Table 5. Densities ρ and Viscosities η for Benzylamine (1) + 2-Methyl-2-butanol (2)

x_1	$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K	
	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$
0.1000	0.8234	3.228	0.8194	2.641	0.8140	2.193
0.2001	0.8421	2.988	0.8378	2.463	0.8329	2.043
0.3000	0.8602	2.781	0.8560	2.289	0.8515	1.919
0.4000	0.8781	2.576	0.8738	2.143	0.8694	1.793
0.5000	0.8954	2.394	0.8910	1.995	0.8866	1.696
0.6000	0.9124	2.223	0.9079	1.882	0.9033	1.609
0.6999	0.9292	2.067	0.9247	1.773	0.9202	1.533
0.7994	0.9458	1.927	0.9412	1.668	0.9368	1.468
0.8998	0.9625	1.792	0.9575	1.578	0.9535	1.422

absolute viscosities with mole fraction of benzylamine x_1 for the mixtures at 303.15 K. The viscosities decrease monotonically with a decrease of x_1 for each binary system.

Excess volumes V^E ($\text{cm}^3\cdot\text{mol}^{-1}$) and viscosity deviations $\delta\eta$ ($\text{mPa}\cdot\text{s}$) were calculated from the experimental results with the following equations:

$$V^E = V_m - (x_1 V_1 + x_2 V_2) \quad (2)$$

$$\delta\eta = \eta_m - (x_1 \eta_1 + x_2 \eta_2) \quad (3)$$

where x_i , V_i , and η_i are the mole fraction, molar volume, and viscosity of the pure component i , respectively. The subscript m represents mixture properties. The composition

Table 6. Densities ρ and Viscosities η for Benzylamine (1) + 3-Methyl-1-butanol (2)

x_1	$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K	
	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$
0.0999	0.8234	3.425	0.8198	2.914	0.8176	2.536
0.1999	0.8428	3.149	0.8391	2.672	0.8359	2.319
0.3000	0.8616	2.901	0.8577	2.455	0.8540	2.142
0.4000	0.8800	2.684	0.8759	2.259	0.8718	1.979
0.5000	0.8976	2.474	0.8935	2.099	0.8893	1.833
0.6000	0.9142	2.284	0.9103	1.937	0.9061	1.706
0.7000	0.9302	2.103	0.9262	1.803	0.9225	1.602
0.8000	0.9466	1.941	0.9424	1.683	0.9386	1.510
0.9000	0.9627	1.806	0.9577	1.582	0.9540	1.441

Table 7. Densities ρ and Viscosities η for Benzylamine (1) + 3-Methyl-2-butanol (2)

x_1	$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K	
	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$
0.0999	0.8320	3.336	0.8278	2.903	0.8240	2.388
0.2000	0.8500	3.109	0.8459	2.663	0.8416	2.184
0.3002	0.8674	2.890	0.8633	2.443	0.8590	2.009
0.4001	0.8842	2.683	0.8801	2.249	0.8760	1.853
0.4997	0.9008	2.490	0.8966	2.084	0.8923	1.724
0.5998	0.9170	2.315	0.9126	1.927	0.9083	1.614
0.6999	0.9329	2.131	0.9284	1.792	0.9239	1.521
0.7997	0.9484	1.960	0.9438	1.673	0.9394	1.449
0.9000	0.9636	1.810	0.9589	1.571	0.9548	1.404

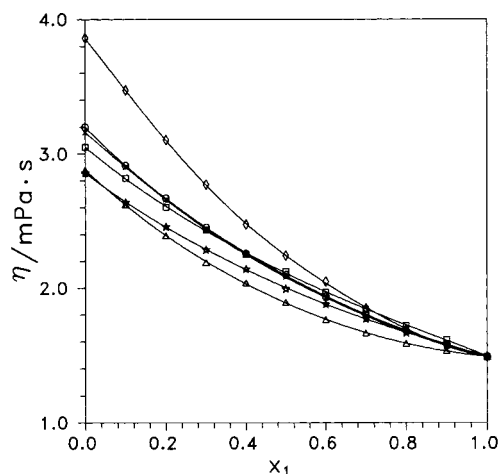


Figure 1. Viscosity at 303.15 K: (\square) benzylamine (1) + 1-pentanol (2); (\triangle) benzylamine (1) + 2-pentanol (2); (\diamond) benzylamine (1) + 2-methyl-1-butanol (2); (\star) benzylamine (1) + 2-methyl-2-butanol (2); (\circ) benzylamine (1) + 3-methyl-1-butanol (2); (\times) benzylamine (1) + 3-methyl-2-butanol (2).

dependence of either the V^E or $\delta\eta$ isotherm was represented by a Redlich–Kister type equation

$$Y = x_1 x_2 \sum_{i=0}^p a_i (x_1 - x_2)^i \quad (4)$$

where Y refers to V^E or $\delta\eta$, and x_1 and x_2 are the mole fractions of benzylamine and the alcohol component, respectively. The coefficients a_i were obtained by fitting eq 4 to the experimental results with a least-squares method. The correlated results are given in Tables 8 and 9, in which the tabulated standard deviation σ was defined

$$\sigma = \left[\frac{\sum (Y_{\text{exp}} - Y_{\text{cal}})^2}{n - p} \right]^{1/2} \quad (5)$$

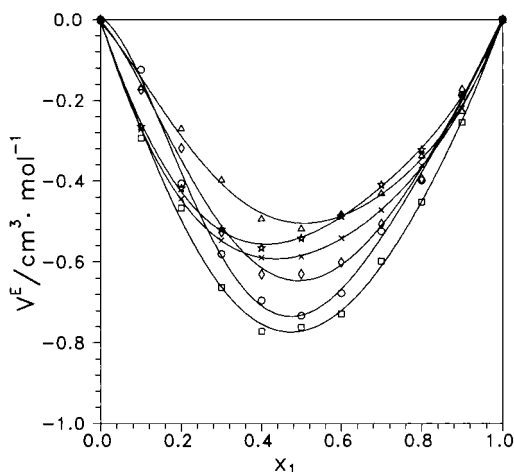
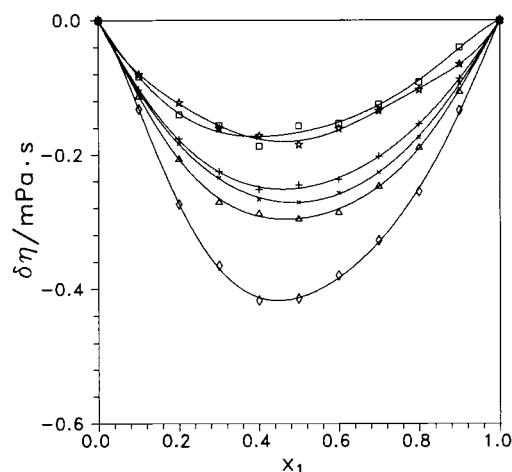
where n is the number of data points and p is the number of coefficients. The subscript cal denotes the correlated value.

Table 8. Correlated Results for Excess Molar Volume V^E

system	T/K	a_0	a_1	a_2	a_3	$10^3\sigma/\text{cm}^3\cdot\text{mol}^{-1}$
benzylamine + 1-pentanol	298.15	-2.7578	0.4934	1.1750	0.8481	0.0959
	303.15	-3.0476	0.2351	0.1282	0.0106	0.1223
	308.15	-2.7170	0.6451	0.5353	0.2060	0.0805
benzylamine + 2-pentanol	298.15	-1.6446	0.1803	0.7209	0.2249	0.0904
	303.15	-1.9708	-0.1183	-0.1740	-0.4791	0.1294
	308.15	-1.8113	0.3508	0.6447	0.2274	0.0415
benzylamine + 2-methyl-1-butanol	298.15	-1.8830	0.3767	0.7675	-1.0308	0.0478
	303.15	-2.5939	-0.1272	1.0238	0.0838	0.1689
	308.15	-2.3563	0.5541	1.8687	-0.8250	0.0586
benzylamine + 2-methyl-2-butanol	298.15	-1.6823	0.8572	0.5656	-0.7518	0.0234
	303.15	-2.1451	0.6525	-0.5396	-0.2340	0.0497
	308.15	-2.0468	1.3771	0.7650	-1.4980	0.0699
benzylamine + 3-methyl-1-butanol	298.15	-2.8532	1.3483	1.3420	-0.6856	0.0868
	303.15	-2.9650	0.5371	1.7857	-1.4898	0.1376
	308.15	-2.2408	-0.1580	1.0251	0.8239	0.0623
benzylamine + 3-methyl-2-butanol	298.15	-1.9478	0.5975	0.3178	0.3697	0.0801
	303.15	-2.3293	0.4926	-0.5996	-0.1914	0.0218
	308.15	-1.8715	0.5620	0.4174	-0.0215	0.0519

Table 9. Correlated Results for Viscosity Deviation $\delta\eta$

system	T/K	a_0	a_1	a_2	a_3	$10^2\sigma/\text{mPa}\cdot\text{s}$
benzylamine + 1-pentanol	298.15	-0.7185	0.1891	0.0254	-0.0691	0.1121
	303.15	-0.6565	0.1968	0.0396	0.1869	0.2600
	308.15	-0.6389	-0.1976	-0.5021	1.1483	0.6050
benzylamine + 2-pentanol	298.15	-1.2304	0.1583	-0.1855	0.0714	0.1311
	303.15	-1.2057	0.1471	-0.0287	-0.0149	0.1763
	308.15	-0.9667	0.0147	-0.0051	0.2180	0.1259
benzylamine + 2-methyl-1-butanol	298.15	-1.9352	0.2050	-0.1769	-0.2948	0.2056
	303.15	-1.7453	0.2381	-0.0507	-0.3677	0.2041
	308.15	-1.3472	0.1299	-0.1504	-0.2466	0.1865
benzylamine + 2-methyl-2-butanol	298.15	-0.7818	0.1266	-0.1893	0.1251	0.0898
	303.15	-0.6718	0.1406	-0.1048	0.0016	0.1741
	308.15	-0.6924	0.0727	0.0443	0.0450	0.1019
benzylamine + 3-methyl-1-butanol	298.15	-0.9169	0.1017	-0.0729	0.0582	0.1301
	303.15	-1.0056	0.1560	-0.0917	0.0786	0.0894
	308.15	-0.9446	0.0907	0.0975	-0.0198	0.1452
benzylamine + 3-methyl-2-butanol	298.15	-0.6718	0.1033	-0.5611	0.4717	0.2130
	303.15	-0.9907	0.1183	0.0298	-0.1381	0.0510
	308.15	-1.0948	0.0438	-0.0312	0.0318	0.0852

**Figure 2.** Excess volumes V^E of benzylamine (1) + pentyl alcohol (2) at 303.15 K: (\square) benzylamine (1) + 1-pentanol (2); (Δ) benzylamine (1) + 2-pentanol (2); (\diamond) benzylamine (1) + 2-methyl-1-butanol (2); (\ast) benzylamine (1) + 2-methyl-2-butanol (2); (\circ) benzylamine (1) + 3-methyl-1-butanol (2); (\times) benzylamine (1) + 3-methyl-2-butanol (2); (—) calculated from eq 4.**Figure 3.** Viscosity deviations $\delta\eta$ of benzylamine (1) + pentyl alcohol (2) at 303.15 K: (\square) benzylamine (1) + 1-pentanol (2); (Δ) benzylamine (1) + 2-pentanol (2); (\diamond) benzylamine (1) + 2-methyl-1-butanol (2); (\ast) benzylamine (1) + 2-methyl-2-butanol (2); (\circ) benzylamine (1) + 3-methyl-1-butanol (2); (\times) benzylamine (1) + 3-methyl-2-butanol (2); (—) calculated from eq 4.

The variations of V^E and $\delta\eta$ with the mole fraction of benzylamine at 303.15 K are presented in Figures 2 and 3, respectively. Figure 2 shows that the excess molar volumes are negative for all these investigated systems. It is implied that volume contraction is taking place when benzylamine mixes with the alcohol isomers. Hydrogen-

bond formation between the OH-group and the NH-group could result in the volume contraction. The sterically hindered effects on the excess molar volumes are also shown in Figure 2. It appears that the alcohols with the OH-group at the end of the molecular chain (such as 1-pentanol, 3-methyl-1-butanol, and 2-methyl-1-butanol)

Table 10. Coefficients for Kinematic Viscosity with McAllister's Models

system	three-body model				four-body model			
	<i>T</i> /K	ν_{12}	ν_{21}	AAD% ^a	ν_{1112}	ν_{1122}	ν_{2221}	AAD% ^a
benzylamine + 1-pentanol	298.15	2.3121	3.0880	0.08	2.1473	2.6606	3.3667	0.08
	303.15	2.0538	2.6626	0.27	1.9202	2.3157	2.9116	0.26
	308.15	1.7621	2.3568	0.49	1.6576	2.0588	2.5527	0.47
benzylamine + 2-pentanol	298.15	2.0790	2.9616	0.18	1.9610	3.0960	4.1023	0.13
	303.15	1.7188	2.4328	0.15	1.6607	2.4744	3.4308	0.14
	308.15	1.5456	2.0871	0.20	1.5189	1.8796	2.4535	0.18
benzylamine + 2-methyl-1-butanol	298.15	2.2935	3.7885	0.31	2.0792	2.5377	3.2051	0.22
	303.15	1.9092	3.1002	0.38	1.7752	2.0622	2.6740	0.35
	308.15	1.4996	2.2343	0.39	1.4396	1.7792	2.2987	0.32
benzylamine + 2-methyl-2-butanol	298.15	2.2734	3.0993	0.17	2.0942	2.7079	3.3142	0.08
	303.15	1.9366	2.5540	0.16	1.8214	2.2352	2.7612	0.15
	308.15	1.6388	2.1345	0.13	1.5800	1.8692	2.3160	0.12
benzylamine + 3-methyl-1-butanol	298.15	2.3159	3.2224	0.15	2.1112	2.7928	3.4991	0.11
	303.15	1.9441	2.7161	0.11	1.8200	2.3176	2.9781	0.09
	308.15	1.6965	2.4018	0.19	1.6463	1.9665	2.6700	0.16
benzylamine + 3-methyl-2-butanol	298.15	2.3811	3.1818	0.46	2.1296	2.8908	3.3694	0.17
	303.15	1.9083	2.7157	0.14	1.7863	2.3140	2.9579	0.10
	308.15	1.5590	2.2261	0.11	1.5105	1.8866	2.4305	0.08

$$^a \text{AAD\%} = (100/n) \sum_{k=1}^n |\nu_k^{\text{cal}} - \nu_k^{\text{exp}}| / \nu_k^{\text{exp}}$$

much more easily form hydrogen-bonds with benzylamine; thus, their excess molar volumes are more negative than those of the other binary systems at near equimolar conditions. Moreover, the excess volumes were found to increase with increasing temperature. Figure 3 illustrates that the viscosity deviations are also negative for each binary system. As evidenced from the calculations, the viscosity deviations decrease with an increase of temperature.

McAllister's multibody interaction model (McAllister, 1960) has been widely used to correlate kinematic viscosities ν . The three-body McAllister model is defined as

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln[x_1 + x_2(M_2/M_1)] + 3x_1^2 x_2 \ln[(2 + M_2/M_1)/3] + 3x_1 x_2^2 \ln[(1 + 2M_2/M_1)/3] + x_2^3 \ln(M_2/M_1) \quad (6)$$

and the four-body model is given by

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln \nu_{1112} + 6x_1^2 x_2^2 \ln \nu_{1122} + 4x_1 x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln[x_1 + x_2(M_2/M_1)] + 4x_1^3 x_2 \ln[(3 + M_2/M_1)/4] + 6x_1^2 x_2^2 \ln[(1 + M_2/M_1)/2] + 4x_1 x_2^3 \ln[(1 + 3M_2/M_1)/4] + x_2^4 \ln(M_2/M_1) \quad (7)$$

where ν_{12} , ν_{21} , ν_{1112} , ν_{1122} , and ν_{2221} are model parameters. The calculated results are presented in Table 10. The average deviations are approximately within the experimental uncertainty, regardless of whether the three-body or the four-body model was used.

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