Densities, Viscosities, and Refractive Indices of the Binary Liquid Systems *n*-Alkanes + Isomers of Hexane at 298.15 K

Antonio Aucejo,* M. Cruz Burguet, Rosa Muñoz, and José L. Marqués

Departamento de Ingeniería Química, Facultad de Química, Universitat de Valencia, 46100 Burjassot, Valencia, Spain

In this paper the viscosities, densities, and refractive indices of nine binary liquid systems containing *n*-alkane + isomers of hexane have been determined at 298.15 K. The viscosity values were fitted to the McAllister three-body model and the Redlich–Kister-type equation. The results with these models agree with experimental data with an average absolute deviation of less than 0.6%.

Introduction

The present paper forms part of our program on the measurement of transport properties (Aucejo et al., 1986, 1995; Orts et al., 1988). Densities, viscosities, and refractive indices of binary mixtures of hexadecane + 2-methylpentane, + 3-methylpentane, + 2,2-dimethylbutane, and + 2,3-dimethylbutane; dodecane + 2-methylpentane, + 2,2-dimethylbutane, and + 2,3-dimethylbutane; and tetradecane + 2-methylpentane and + 2,3-dimethylbutane are reported at 298.15 K.

Experimental Section

All the chemicals used in the present study were supplied by Aldrich Chemical Co. and were used as received. No further purification treatment was carried out. The stated purity of all the chemicals exceeded 99 mass % except for the purity of 2,3-dimethylbutane which was higher than 98.0 mass %.

All the solutions were prepared using a Mettler balance with an accuracy of ±0.0001 g. Densities of the pure components and their mixtures were measured with an Anton Paar (model DMA 55) densimeter with a resolution of 2×10^{-5} g·cm^{-3}. The density determination is based on measuring the period of oscillation of the vibrating U-shaped sample tube filled with the sample. The temperature of the thermostat was maintained constant to within ±0.01 K. Temperatures were detected with a digital precision thermometer (Anton Paar DT 100-20).

An Ubbelohde viscometer was used for determining the viscosities of pure liquids and the binary systems. The apparatus was submerged in a thermostatic bath at 25 °C with a resolution of ±0.1 °C. The viscometer was calibrated with pure components whose viscosity and density were well known, as has been described in a previous paper (Aucejo et al., 1986). Viscosity values were determined using the relation (Wright, 1961; Mulcahy, 1984)

$$\eta/\varrho = At - B/t \qquad (1)$$

where η is the viscosity, ϱ is the liquid density, t is its flow time in the viscometer, and A and B are viscometer constants, determined for measurements with calibration fluids. Each experimental point is the average of 10 measurements with a maximum deviation of ±0.2% in flow time.

No changes in the composition were observed on comparing the value of the refractive index before and after the viscosity measurement. The refractive indices were measured with an Abbe refractometer (type 3T) with an accuracy of ±0.0002.

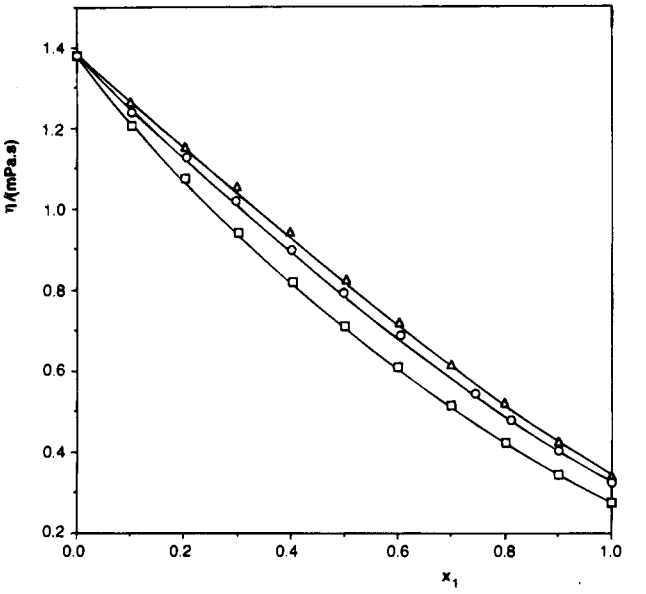

Figure 1. Viscosities of 2-methylpentane (1) + dodecane (2), □; 2,2-dimethylbutane (1) + dodecane (2), △; and 2,3-dimethylbutane (1) + dodecane (2), ○.

Results and Discussion

The experimental densities, refractive indices, and viscosities of the nine binary mixtures are shown in Table 1, as well as the excess molar volumes (V^E) and the deviation in viscosities ($\Delta\eta$).

Experimental viscosities changed monotonically with composition for all systems. Figure 1 shows, as an illustration, the viscosity–composition results for isomers of hexane (1) + dodecane (2) systems.

The excess molar volumes, V^E, were calculated with the following equation:

$$V^E = V - \sum x_i V_i \qquad (2)$$

where V is the molar volume of the mixture and x_i and V_i are the mole fractions and molar volumes of the pure components, respectively. The excess molar volumes for

0021-9568/95/1740-0871$09.00/0

Table 1. Mole Fractions, x_1, Densities, ϱ, Viscosities, η, Refractive Indices, n_D, Excess Volumes, V^E, and Viscosity Deviation, $\Delta\eta$, for Binary Mixtures

x_1	ϱ/(g·cm^{-3})	η/(mPa·s)	n_D	V^E/(cm^3·mol^{-1})	$\Delta\eta$/(mPa·s)	x_1	ϱ/(g·cm^{-3})	η/(mPa·s)	n_D	V^E/(cm^3·mol^{-1})	$\Delta\eta$/(mPa·s)
2-Methylpentane (1) + Hexadecane (2)											
0.0000	0.769 81	3.0930	1.4334	0.0000	1.0000	0.6029	0.723 78	0.9821	1.4096	−0.9002	1.3651
0.1177	0.763 79	2.5724	1.4310	−0.3143	1.1056	0.7034	0.710 61	0.7606	1.4026	−0.8949	1.3482
0.2071	0.758 28	2.1986	1.4280	−0.4361	1.1731	0.8025	0.694 47	0.5679	1.3940	−0.7491	1.2792
0.3082	0.751 20	1.8346	1.4245	−0.5553	1.2501	0.9006	0.674 39	0.3949	1.3830	−0.4505	1.1279
0.4013	0.743 82	1.5304	1.4204	−0.6762	1.3062	1.0000	0.648 54	0.2753	1.3688	0.0000	1.0000
0.4982	0.735 03	1.2411	1.4152	−0.8040	1.3391						
3-Methylpentane (1) + Hexadecane (2)											
0.0000	0.769 81	3.0930	1.4334	0.0000	1.0000	0.6034	0.727 84	1.0217	1.4108	−0.6552	1.3837
0.1071	0.764 92	2.6353	1.4313	−0.2470	1.0987	0.7044	0.715 79	0.7813	1.4050	−0.6513	1.3447
0.2084	0.759 29	2.2239	1.4287	−0.3472	1.1792	0.8037	0.701 07	0.5939	1.3969	−0.5393	1.2939
0.3095	0.752 82	1.8704	1.4255	−0.4178	1.2608	0.9020	0.682 78	0.4194	1.3869	−0.3140	1.1540
0.4069	0.745 72	1.5538	1.4211	−0.4992	1.3198	1.0000	0.659 67	0.2880	1.3742	0.0000	1.0000
0.5054	0.737 49	1.2744	1.4168	−0.5898	1.3676						
2,2-Dimethylbutane (1) + Hexadecane (2)											
0.0000	0.769 81	3.0930	1.4334	0.0000	1.0000	0.6057	0.722 21	1.2107	1.4090	−1.0519	1.4893
0.1107	0.764 34	2.7355	1.4310	−0.4438	1.1290	0.7048	0.708 85	0.9511	1.4017	−1.0657	1.4559
0.2098	0.758 10	2.4050	1.4278	−0.6076	1.2352	0.8022	0.692 54	0.7110	1.3930	−0.9247	1.3493
0.3108	0.750 70	2.0707	1.4236	−0.7088	1.3290	0.9014	0.671 53	0.5046	1.3813	−0.5792	1.1917
0.4014	0.743 20	1.7875	1.4202	−0.8101	1.4010	1.0000	0.644 65	0.3406	1.3661	0.0000	1.0000
0.5013	0.733 79	1.4860	1.4148	−0.9401	1.4519						
2,3-Dimethylbutane (1) + Hexadecane (2)											
0.0000	0.769 81	3.0930	1.4334	0.0000	1.0000	0.6023	0.727 18	1.1350	1.4116	−0.7556	1.4257
0.0846	0.766 10	2.7734	1.4315	−0.2749	1.0850	0.7034	0.714 87	0.8764	1.4053	−0.7514	1.3825
0.2077	0.759 24	2.3253	1.4288	−0.4207	1.2005	0.8019	0.699 98	0.6623	1.3973	−0.6317	1.3044
0.2966	0.753 55	2.0452	1.4253	−0.5164	1.2901	0.9002	0.681 28	0.4751	1.3860	−0.3798	1.1676
0.3988	0.746 02	1.7402	1.4213	−0.5953	1.3819	1.0000	0.657 08	0.3249	1.3720	0.0000	1.0000
0.4973	0.737 67	1.4317	1.4170	−0.6834	1.4195						
2-Methylpentane (1) + Dodecane (2)											
0.0000	0.745 03	1.3791	1.4196	0.0000	1.0000	0.6002	0.702 80	0.6097	1.3976	−0.6649	1.1628
0.1004	0.740 10	1.2050	1.4172	−0.3163	1.0304	0.6996	0.692 26	0.5148	1.3922	−0.6356	1.1525
0.2007	0.734 18	1.0752	1.4142	−0.4101	1.0773	0.8002	0.680 02	0.4229	1.3852	−0.5552	1.1133
0.3018	0.727 52	0.9390	1.4108	−0.5116	1.1073	0.9003	0.665 51	0.3443	1.3778	−0.3268	1.0649
0.4027	0.720 12	0.8181	1.4068	−0.5950	1.1350	1.0000	0.648 54	0.2753	1.3688	0.0000	1.0000
0.5008	0.712 00	0.7124	1.4026	−0.6364	1.1576						
2,2-Dimethylbutane (1) + Dodecane (2)											
0.0000	0.745 03	1.3791	1.4196	0.0000	1.0000	0.6011	0.701 79	0.7202	1.3974	−0.9233	1.2104
0.0995	0.740 12	1.2635	1.4170	−0.3499	1.0529	0.7000	0.690 82	0.6152	1.3912	−0.8717	1.1872
0.2015	0.734 07	1.1520	1.4140	−0.5555	1.1072	0.7997	0.678 09	0.5206	1.3848	−0.7511	1.1551
0.2997	0.727 46	1.0556	1.4104	−0.6936	1.1639	0.9002	0.662 69	0.4256	1.3762	−0.4408	1.0866
0.3975	0.720 23	0.9440	1.4070	−0.8330	1.1934	1.0000	0.644 65	0.3406	1.3661	0.0000	1.0000
0.5013	0.711 42	0.8256	1.4025	−0.9029	1.2067						
2,3-Dimethylbutane (1) + Dodecane (2)											
0.0000	0.745 03	1.3791	1.4196	0.0000	1.0000	0.6035	0.706 13	0.6871	1.3984	−0.5040	1.1920
0.1010	0.740 36	1.2370	1.4166	-0.1935	1.0379	0.7426	0.692 10	0.5433	1.3913	−0.4274	1.1525
0.2039	0.734 98	1.1268	1.4136	−0.3455	1.0971	0.8116	0.684 00	0.4795	1.3867	−0.3459	1.1239
0.2970	0.729 47	1.0180	1.4108	−0.4370	1.1340	0.9014	0.672 14	0.4023	1.3805	−0.2042	1.0738
0.4013	0.722 43	0.8980	1.4072	−0.4788	1.1631	1.0000	0.657 08	0.3249	1.3720	0.0000	1.0000
0.4985	0.715 09	0.7936	1.4033	−0.5031	1.1829						
2-Methylpentane (1) + Tetradecane (2)											
0.0000	0.759 06	2.0743	1.4268	0.0000	1.0000	0.6012	0.714 60	0.7806	1.4035	−0.8997	1.2671
0.1041	0.753 59	1.7946	1.4239	−0.2285	1.0676	0.7022	0.702 32	0.6276	1.3973	−0.8565	1.2493
0.2003	0.748 01	1.5953	1.4209	−0.4515	1.1525	0.8003	0.688 07	0.4899	1.3898	−0.7241	1.1889
0.3021	0.741 41	1.3624	1.4174	−0.6857	1.2089	0.8985	0.670 59	0.3762	1.3803	−0.4257	1.1132
0.4053	0.733 38	1.1364	1.4132	−0.7873	1.2420	1.0000	0.648 54	0.2753	1.3688	0.0000	1.0000
0.5024	0.724 71	0.9502	1.4089	−0.8519	1.2636						
2,3-Dimethylbutane (1) + Tetradecane (2)											
0.0000	0.759 06	2.0743	1.4268	0.0000	1.0000	0.6031	0.717 65	0.8719	1.4048	−0.6898	1.2858
0.1000	0.754 04	1.8838	1.4242	−0.1203	1.0931	0.7010	0.706 48	0.7123	1.3990	−0.6122	1.2595
0.2006	0.748 54	1.6686	1.4216	−0.2780	1.1667	0.8016	0.693 06	0.5711	1.3917	−0.5195	1.2167
0.3044	0.742 27	1.4515	1.4178	−0.4693	1.2303	0.9008	0.676 81	0.4356	1.3828	−0.2930	1.1154
0.4033	0.735 40	1.2458	1.4140	−0.6153	1.2684	1.0000	0.657 08	0.3249	1.3720	0.0000	1.0000
0.5030	0.727 18	1.0506	1.4095	−0.6643	1.2869						

all the binary mixtures are negative over the whole mole fraction range at 298.15 K. They become more negative as the length of the *n*-alkane involved in the mixture increases. Figure 2 shows, as an illustration, the excess molar volume−composition results for isomers of hexane (1) + dodecane (2) systems together with the excess molar volume of the *n*-hexane (1) + dodecane (2) system (Aucejo et al., 1995).

Table 2. Coefficients of the Redlich–Kister-Type Equation for Excess Molar Volume, V^E

system	B_0	B_1	B_2	B_3	AAD[a]/%
2-methylpentane (1) + hexadecane (2)	−3.2231	2.4004	−1.3288	−1.9158	0.0004
3-methylpentane (1) + hexadecane (2)	−2.3424	1.7353	−1.1827	−1.8291	0.0003
2,2-dimethylbutane (1) + hexadecane (2)	−3.7526	2.5487	−2.8320	−2.1854	0.0007
2,3-dimethylbutane (1) + hexadecane (2)	−2.7511	1.7414	−1.5869	−1.8322	0.0016
2-methylpentane (1) + dodecane (2)	−2.5487	0.9267	−1.2615	−0.7716	0.0042
2,2-dimethylbutane (1) + dodecane (2)	−3.5918	1.1593	−1.2439	−0.6671	0.0055
2,3-dimethylbutane (1) + dodecane (2)	−2.0409	0.1775	−0.3909	−0.1504	0.0032
2-methylpentane (1) + tetradecane (2)	−3.5011	1.0878	−0.3859	0.6106	0.0082
2,3-dimethylbutane (1) + tetradecane (2)	−2.6940	0.8642	0.6010	0.7311	0.0056

[a] AAD = $[\sum_1^N(|V_{exptl} - V_{calc}|/V_{exptl})100]/N$ (N = number data points).

Table 3. Coefficients of the Redlich–Kister-Type Equation for Viscosity Deviation, $\Delta\eta$

system	C_0	C_1	C_2	C_3	AAD[a]/%
2-methylpentane (1) + hexadecane (2)	1.4025	−0.7531	−0.1033	0.6651	0.61
3-methylpentane (1) + hexadecane (2)	1.4584	−0.6733	−0.0608	0.2727	0.35
2,2-dimethylbutane (1) + hexadecane (2)	1.8481	−0.9263	−0.1194	0.6556	0.32
2,3-dimethylbutane (1) + hexadecane (2)	1.6849	−0.5592	−0.3396	0.0612	0.32
2-methylpentane (1) + dodecane (2)	0.6312	−0.2594	−0.1379	0.0564	0.24
2,2-dimethylbutane (1) + dodecane (2)	0.8417	−0.1478	−0.0765	−0.1779	0.24
2,3-dimethylbutane (1) + dodecane (2)	0.7428	−0.1997	−0.1511	−0.0313	0.28
2-methylpentane (1) + tetradecane (2)	1.0698	−0.2156	−0.0480	−0.0980	0.42
2,3-dimethylbutane (1) + tetradecane (2)	1.1511	−0.2237	0.0763	0.0293	0.24

[a] AAD = $[\sum_1^N(|\eta_{exptl} - \eta_{calc}|/\eta_{exptl})100]/N$ (N = number data points).

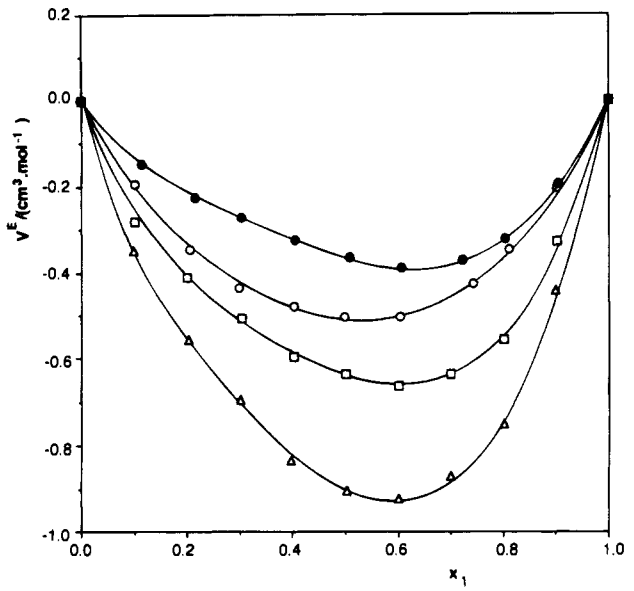

Figure 2. Excess volumes of 2-methylpentane (1) + dodecane (2), □; 2,2-dimethylbutane (1) + dodecane (2), △; 2,3-dimethylbutane (1) + dodecane (2), ○; and n-hexane (1) + dodecane (2), ●. The solid curves have been calculated from eq 3.

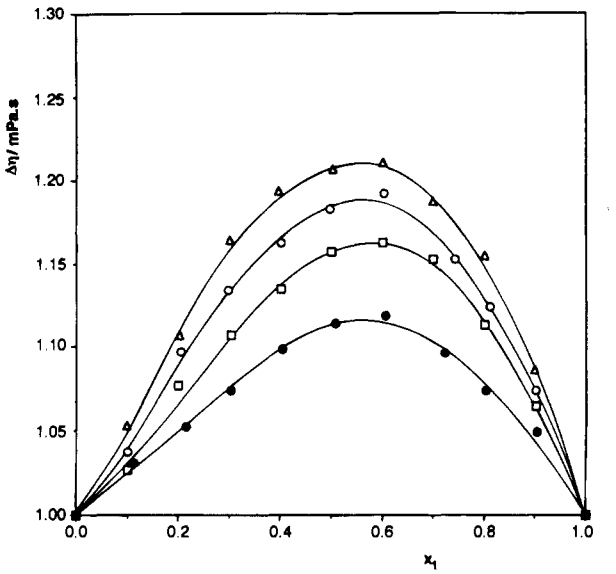

Figure 3. Viscosity deviations of 2-methylpentane (1) + dodecane (2), □; 2,2-dimethylbutane (1) + dodecane (2), △; 2,3-dimethylbutane (1) + dodecane (2), ○; and n-hexane (1) + dodecane (2), ●. The solid curves have been calculated from eq 5.

The excess molar volumes were fitted to a Redlich–Kister-type equation:

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1x_2\sum_{i=0}^{3}B_i(x_2 - x_1)^i \qquad (3)$$

The values of the adjustable parameters B_i included in eq 3 were determined for the systems studied using a least squares method. These values are reported in Table 2 together with the average absolute deviation (AAD).

The viscosity deviations, $\Delta\eta$, were calculated with the expression proposed by Ratcliff and Khan (1971):

$$\ln \Delta\eta = \ln \eta - \sum x_i \ln \eta_i \qquad (4)$$

where η is the viscosity of the mixture and x_i and η_i are the mole fractions and the viscosity of the pure components, respectively. It can be observed that deviations from ideality are greater as the number of chains and their proximity increase. Figure 3 shows, as an illustration, the viscosity deviation–composition results for isomers of hexane (1) + dodecane (2) systems together with the viscosity deviation of n-hexane (1) + dodecane (2) system (Aucejo et al., 1995).

A Redlich–Kister-type equation and the McAllister three-body model (1960) have been used to fit the experimental viscosity–composition data. The Redlich–Kister-type equation is

$$(\Delta\eta - 1)/(\text{mPa·s}) = x_1x_2\sum_{i=0}^{3}C_i(x_2 - x_1)^i \qquad (5)$$

The values of the adjustable parameters C_i included in eq 5 were determined for the systems studied using a least

Table 4. Coefficients of the McAllister Three-Body Model for Kinematic Viscosity, ν

system	ν_{12}/(mm^2·s^{-1})	ν_{21}/(mm^2·s^{-1})	AAD[a]/%
2-methylpentane (1) + hexadecane (2)	1.5554	4.2220	0.62
3-methylpentane (1) + hexadecane (2)	1.6564	4.2124	0.43
2,2-dimethylbutane (1) + hexadecane (2)	2.1119	4.7975	0.47
2,3-dimethylbutane (1) + hexadecane (2)	1.8515	4.6992	0.24
2-methylpentane (1) + dodecane (2)	0.9069	2.0906	0.26
2,2,dimethylbutane (1) + dodecane (2)	1.0954	2.4078	0.24
2,3-dimethylbutane (1) + dodecane (2)	1.0149	2.3278	0.22
2-methylpentane (1) + tetradecane (2)	1.1680	3.1193	0.38
2,3-dimethylbutane (1) + tetradecane (2)	1.3047	3.4946	0.47

[a] AAD = $[\sum_1^N(|\nu_{exptl} - \nu_{calc}|/\nu_{exptl})100]/N$ (N = number data points).

squares method. These values are reported in Table 3 together with the average absolute deviation (AAD). The McAllister three-body model is given by the equation

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

where ν_m is the kinematic viscosity of the mixture, x_i , ν_i, and M_i are the mole fractions, the kinematic viscosity, and the molar mass of the pure components, respectively, and ν_{12} and ν_{21} are the interaction parameters.

The values of the adjustable parameters ν_{12} and ν_{21} included in eq 6 were determined for the systems studied using a least squares method. These values are reported in Table 4 together with the average absolute deviation (AAD).

The AAD of all fits indicates that the models given by eqs 3, 5, and 6 fit the experimental data very well. It can be observed in Figures 2 and 3 that *n*-hexane behavior is closer to ideality than those of the more branched isomers.

Literature Cited

Aucejo, A.; Part, E.; Medina, P.; Sanchotello, M. Viscosity of Some *n*-Alkane/1-Chloroalkane Binary Mixtures. *J. Chem. Eng. Data* **1986**, *31*, 143–145.

Aucejo, A.; Burguet, M. C.; Muñoz, R.; Marqués, J. Densities, Viscosities, and Refractive Indices of Some *n*-Alkane Binary Liquid Systems at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 141–147.

McAllister, R. A. The viscosity of liquid mixtures. *AIChE J.* **1960**, *6*, 427–431.

Mulcahy, D. E. Flow equation for a Hared-capillary Viscosimeter. *J. Phys. D: Appl. Phys.* **1984**, *17*, 219–223.

Orts, M. J.; Medina, P.; Aucejo, A.; Burguet, M. C. Viscosity of n-alcohol binary mixtures. *Can. J. Chem. Eng.* **1988**, *66*, 651–655.

Ratcliff, G. A.; Khan, M. A. Prediction of the viscosities of liquid mixtures by a group solution model. *Can. J. Chem. Eng.* **1971**, *49*, 125–129.

Wright, F. J. Influence of Temperature on Viscosity of Nonassociated Liquids. *J. Chem. Eng. Data* **1961**, *6*, 454–456.

Received for review December 6, 1994. Accepted March 17, 1995.[⊗] This work was supported by the CAICYT, Project PA85-0076.

JE940262E

[⊗] Abstract published in *Advance ACS Abstracts*, May 15, 1995.