200. Physico-Chemical Properties of Deuteriated Compounds

3rd Communication[1])

The Viscosity of n-Heptane

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Summary. The kinematic viscosity of mixtures of perdeuteriated and protiated heptane has been measured between 15° and 35° and is given in polynomial form as a function of concentration and temperature. Using the *McAllister* equation to describe viscosity [4], it can be shown that the interactions between molecules containing the same or different isotopic species differ slightly.

1. Introduction. – In a previous publication in this series [2] we showed that the molar volume of mixtures of protiated and deuteriated n-heptane is a non-linear function of their composition. In order to examine more closely this slight irregularity of isotopic mixtures, we measured the viscosity of the same solutions over a limited temperature range. The viscosity of D_2O/H_2O-mixtures has attracted much interest and has been reviewed by *Jansco* & van *Hook* [3], but corresponding information regarding hydrocarbon mixtures is lacking.

2. Experimental. – The n-heptanes used were carefully distilled; no impurities could be detected by gas chromatography in the protiated (*Phillips* Research Grade) or in the deuteriated (99.6% degree of deuteriation) heptane. Viscosities were measured with a '*Viscomatic*' automatic viscometer FICA using an '*Ubbelohde*' viscometric tube (Société française d'instruments de contrôle et d'analyses). Temperature was measured with a quartz thermometer (*Hewlett Packard* 2801 A). *Phillips* Research grade hydrocarbons were used for calibration of the viscometer, for which the constants were determined from the following relationship:

$$v = \eta/d = A \cdot t - (B/t) \tag{1}$$

where the parameters A and B depend on temperature; v, η, d and t are the kinematic viscosity, the absolute viscosity, the density and the elution time, respectively. The temperature did not vary by more than $\pm 0.005°$ during a single measurement nor by more than $\pm 0.02°$ during the period required to measure any one series of solutions of varying concentrations. The results for 17 concentrations were subsequently corrected to a common temperature.

The average deviation from the viscosity given by (1) is $2–3 \cdot 10^{-3}$ for temperatures between $+15°$ and 35°. We therefore assume our results to be accurate to $\pm 0.3\%$. It will be shown below that our values are reproducible with an accuracy of one fifth of this. The concentrations of the mixtures obtained by weighing the pure compounds were checked by gas chromatography.

3. Results. – 3.1. *The kinematic viscosity.* The measurement of free flow time in a capillary viscometer permits the calculation of the kinematic viscosity v. Several different polynomials were fitted to the results. As the fits obtained did not differ appreciably, we decided to use an equation containing terms up to the second degree in the molar fraction x and in temperature, with 25° taken as the origin. The equation for v in cSt is:

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[1]   2nd Commun. see [1].

$$\nu = 0.5802 - 0.0508 \cdot x + 0.0110 \cdot x^2 - (5.72 - 0.10 \cdot x - 0.32 \cdot x^2) \cdot 10^{-3}(T - 25^\circ)$$
$$+ (74 - 13x + 4 \cdot x^2) \cdot 10^{-6}(T - 25^\circ)^2$$

for $15^\circ \leqslant T \leqslant 35^\circ; 0 \leqslant x \leqslant 1$ $\qquad\qquad$ (2)

Polynomials of higher degree did not significantly improve the results because of the small number of mixtures measured. When measuring the molar volumes, expressing the concentration in weight fractions instead of mole fractions reduced the degree of the polynomial needed for good accord with results. This was not the case for the viscosity data.

Eq. (2) reproduces the measured results with a standard deviation of $5 \cdot 10^{-4}$ for a single measurement and a standard error of $6 \cdot 10^{-5}$ for the regression. As pointed out in the experimental section, a greater error in the absolute accuracy of the results must be allowed for. The viscosity of deuteriated heptane is smaller than that for the protiated hydrocarbon. An increase of 8° in the temperature of the protiated heptane has roughly the same effect as complete deuteriation. The decrease in viscosity caused by deuteriation is, to a first approximation, linear in the mole fraction, but the quadratic term is nevertheless significantly different from zero.

3.2. *The absolute viscosity.* The product of the kinematic viscosity ν and the density of the solution d is the absolute viscosity, values for which were calculated from the density values given in [2]. In polynominal form, η, (in cP), can be expressed as:

$$\eta = 0.3941 + 0.0287 \cdot x + 0.0040 \cdot x^2 - (4.43 + 0.65x - 0.29 \cdot x^2) \cdot 10^{-3}(T - 25)$$
$$+ 57.10^{-6}(T - 25)^2$$ $\qquad\qquad$ (3)

The range of the variables, the standard deviation and the standard error, are the same as for eq. (2); however the equation needs fewer terms to give η to the same accuracy. The best estimates for the viscosities of protiated and deuteriated heptane are nevertheless obtained by separate treatment of measurements made at different temperatures. These results are given in table 1.

Table 1. *The viscosity values for* n-C_7H_{16} *and* n-C_7D_{16}

T°	kin. viscosity ν in cSt		abs. viscosity η in cP	
	C_7H_{16}	C_7D_{16}	C_7H_{16}	C_7D_{16}
15.46	0.6417	0.5971	0.4417	0.4779
20.18	0.6095	0.5674	0.4169	0.4516
24.42	0.5823	0.5423	0.3956	0.4282
29.91	0.5554	0.5175	0.3751	0.4062
34.57	0.5316	0.4949	0.3568	0.3861

Assuming that the theory of the rate process is applicable, the temperature dependence of the viscosity can also be expressed by the following equation:

$$\eta_i = A \cdot \exp(B/T) = (hN/V) \exp(\Delta S_i/R) \cdot \exp(\Delta H_i/RT) \qquad\qquad (4)$$

where i is 0 for the protiated and 1 for the deuteriated molecules. The enthalpies and entropies obtained are the same for both liquids $(8.2 \pm 0.2 \text{ kJ/mol})$; the entropy values obtained are $\Delta S_0 = 1.32 \pm 0.02$ and $\Delta S_1 = 1.30$ J/K $\cdot$ mol.

4. Discussion. – A treatment of the viscosity data of binary mixtures has been proposed by *McAllister* [4]. In its simplest form a linear model for the viscosity is

assumed where a molecule i has to be squeezed between two neighbouring molecules j and k. One can assume different interactions for the resulting combination k-i-j, where i, j and k can again have the value 0 (protiated compound) or 1 (deuteriated compounds). This leads to a polynomial of the third degree in concentration, the four coefficients of which are related to the four types of interactions to which a viscosity is assigned:

$$\nu_0: 0 - 0 - 0;\ \nu_{01}: 0 - 1 - 0,1 - 0 - 0;\ \nu_{10}: 1 - 0 - 1,0 - 1 - 1;\ \nu_1: 1 - 1 - 1.$$

The polynomial given by *McAllister* can be transformed to the following form:

$$\ln \nu(x,\ T) + \ln((M_0 + x(M_1 - M_0))/M_0) = b_0(T) + b_1(T) \cdot x + b_2(T) \cdot x^2 + b_3(T) \cdot x^3 \quad (5)$$

where M_1 is the molecular weight. The four different viscosities are given by the following equations:

$$\ln\nu_0 = b_0;\ \ln\nu_{01} = b_0 + b_1/3 - \ln((2M_0 + M_1)/3M_0);\ \ln\nu_{10} = b_0 + 2b_1/3 + b_2/3 - \ln((M_0 + 2M_1)/3M_0);\ \ln\nu_1 = b_0 + b_1 + b_2 + b_3.$$

The values for these viscosities are presented in table 2 together with the entropy and the enthalpy values obtained by using an equation similar to eq. (4) to express the temperature dependence. The standard errors for the values of $\ln\nu_i$ are $\pm 3 \cdot 10^{-4}$. The enthalpy values for C_7H_{16} and C_7D_{16} are identical within the limits of error and amount to 6.94 kJ/mol (Table 2). The two interaction terms are also identical and

Table 2. *Some derived thermodynamic quantities for the kinematic viscosity in* n-C_7H_{16} – n-C_7D_{16} *mixtures*

	ν_0	ν_{01}	ν_{10}	ν_1
$\ln\nu_i$ (25°) $\pm 3 \cdot 10^{-4}$	− 0.5411	− 0.5708	− 0.5920	− 0.4651
$\Delta H/[kJ/mol]$ ± 0.03	6.96	7.11	7.13	6.92
$\Delta S/[J/K \cdot mol]$ $\pm 4 \cdot 10^{-3}$	1.061	1.087	1.095	1.026

The errors given correspond to the standard error obtained by assuming a linear relationship.

equal to 7.12 kJ/mol, which is slightly higher than the values for the protiated hydrocarbon. A similar observation can be made for the entropy of the two interactions with an average value of 1.09 J/K · mol. Our results can be interpreted to mean that a slightly higher energy is required for a molecule to pass between two molecules of different than two of the same species. The results resemble measurements of the molar volumes of similar mixtures, in which it was found that the solution molar volume was slightly smaller than predicted on the basis of a linear relationship with the concentration. Nevertheless, further measurements are needed to confirm these interpretations.

REFERENCES

[1] G. *Dessauges* & T. *Gäumann*, Helv. *59*, 1930 (1976).
[2] H. *Öz* & T. *Gäumann*, Helv. *58*, 2267 (1975).
[3] G. *Jansco* & W. A. *van Hook*, Chem. Rev. *74*, 689 (1974).
[4] R. A. *McAllister*, Amer. Inst. chem. Eng. J. *6*, 427 (1960).