Table IV. Activity Coefficients and Excess Gibbs Free Energy of Mixing for Acetone (1)–Dimethyl Sulfoxide (2) at 30° C.

| Mole Fraction, $X_1$ | Logarithms of Activity Coefficients |  | Excess Gibbs Free Energy, $\Delta G^e_M$ |  |
|---|---|---|---|---|
|  | $\ln f_1$ | $\ln f_2$ | Exptl. | Calcd. regular |
| 0.000 | . . . | 0.000 | 0 | 0 |
| 0.100 | 0.634 | 0.006 | 41 | 60 |
| 0.200 | 0.552 | 0.020 | 76 | 106 |
| 0.300 | 0.476 | 0.039 | 103 | 139 |
| 0.400 | 0.403 | 0.081 | 126 | 158 |
| 0.500 | 0.331 | 0.135 | 140 | 164 |
| 0.600 | 0.259 | 0.225 | 148 | 157 |
| 0.700 | 0.188 | 0.355 | 143 | 137 |
| 0.800 | 0.116 | 0.571 | 125 | 104 |
| 0.900 | 0.045 | 1.018 | 86 | 58 |
| 1.000 | 0.000 | . . . | 0 | 0 |

tions were not known with sufficient accuracy to calculate a reliable excess volume from the density measurements. The negative excess volumes reported here have recently been confirmed (*6*) to within 0.10 ml. mole$^{-1}$.

The Rayleigh scattering data were analyzed as described earlier (*18*) to obtain activity coefficients and excess free energies of mixing of the acetone–dimethyl sulfoxide solutions at 30°. The natural logarithms of the activity coefficients and excess free energies are given at 0.1-mole fraction intervals in Table IV. The excess free energies are compared with calculated values from regular solution theory

$$\Delta G^e_m \text{ regular} = (X_1 V_1^\circ + X_2 V_2^\circ)\phi_1\phi_2(\delta_1 - \delta_2)^2$$

using values of molar volume, $V^\circ$, and solubility parameter, $\delta$, from Table I, mole fraction, $X$, and volume fraction, $\phi$. The experimental value is about 15% less than that predicted by regular solution theory at 0.5 mole fraction. The near success of regular solution theory would be surprising for such polar molecules if they were not so similar in polarity. The free energy is unsymmetrical, being lower than predicted at the dimethyl sulfoxide-rich end and higher than predicted at the acetone-rich end. Combining the free energy of mixing at 0.5 mole fraction with the reported (*2*) heat of mixing of −80 cal. mole$^{-1}$, one obtains the excess entropy of mixing of −0.73 e.u.

## ACKNOWLEDGMENT

The authors thank M. E. Derrick and R. S. Myers for repeating several of the density and excess volume determinations and the Emory Biomedical Data and Analysis Center for use of the computer.

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RECEIVED for review August 6, 1969. Accepted March 3, 1970. Investigation supported by research grant GP-5937 from the National Science Foundation. Miss Haynes was an undergraduate research participant supported by Grant GY-2684 from the National Science Foundation.

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# Some Properties of the Systems 1-Chlorobutane–1-Chlorooctadecane and 1-Chlorobutane–1-Chlorohexane at 25° C.

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Previous work (*9*) has shown that for mixtures of component pairs of considerably differing chain length, there is poor correlation between volumetric and viscometric behavior. The present investigation was undertaken to compare viscosities in two systems where the dissimilarity in chain lengths between the component pairs was significantly different, and where there was little volume change on mixing. Thus viscous behavior described here is essentially free of volumetric aspects. The systems are 1-chlorobutane–1-chlorohexane and 1-chlorobutane–1-chlorooctadecane (denoted here as $C_4Cl$-$C_6Cl$ and $C_4Cl$-$C_{18}Cl$).

For the system $C_4Cl$-$C_{18}Cl$, density and refractive index data are combined to characterize refractivity intercepts in mixtures of 1-chloroalkanes within those homolog limits at 25° C.

## EXPERIMENTAL

**Equipment.** The equipment and techniques parallel those of earlier work (*9, 10*). A water bath thermostatically controlled to ±0.01° C. was used. Bath temperature was monitored with a Beckman thermometer which had been set

**Viscometric, volumetric, and refractometric data are presented for the system 1-chlorobutane–1-chlorooctadecane at 25° C. Only the viscometric properties depart significantly from ideal mixture properties. Viscometric data are also presented for the system 1-chlorobutane–1-chlorohexane at 25° C., which exhibits only a small departure from ideal viscous behavior.**

with a calibrated thermometer. The calibration of the latter was against an NBS certified standard. Times were measured with an electric stop clock which had been calibrated against an electronic time standard. The cathetometer used in pycnometric density determinations indicated height to ±0.05 mm. All weighings were made with a Mettler 300-gram-capacity precision balance with certified balance weights.

Viscosities were determined with a Cannon-Fenske ASTM 50 viscometer. NBS oils of certified viscosity were employed as primary calibration standards. Kinetic energy corrections compared favorably with those predicted for the given capillary diameter (*18*).

Densities were measured with a 4.5-ml. Lipkin pycnometer with precision-bore capillary arms of 1-mm. i.d. The pycnometer was calibrated with distilled water, with heights of the liquid in the capillary arms measured relative to a single etched mark on each arm. Both in calibration and in use with the liquids studied, a length of less than 1 cm. of the capillary was utilized for the equilibrium position of the height of the liquid in the capillary. This was accomplished by loading the pycnometer with a volume of liquid slightly in excess of that needed, and then emptying the excess until the amount remaining reached a reference mark. With this restriction the standard error in calibrated volume *vs.* capillary height was reduced to ±0.00007 ml. Replication of measured densities of the pure components indicate a standard error of ±0.00003 gram per ml. in density, equivalent to ±0.004 to 0.013 ml. per mole for the components of least and greatest molar volume, respectively.

The viscometer and pycnometer were maintained in the bath until constant flow time or liquid volume, respectively, was obtained. As room temperature was only slightly lower than 25° C., temperature equilibrium was established rapidly. Evaporation losses were negligible, from both pycnometer and viscometers.

Liquids were mixed in a 50-ml. modified glass syringe sealed by glass at the needle end. Again evaporation rates were negligible. Transfer to the viscometer and pycnometer was by overpressure through capillary tubing installed within the syringe plunger. The glass equipment was provided with ball and socket joints to minimize evaporation on transfer. Joints were treated with hexane to remove traces of nonvolatile components.

Refractive indices were measured with a Bausch and Lomb Precision refractometer, thermostated at 25.00° ± 0.01° C. and using the sodium-*D* line.

**Materials.** Purification of the components has been described, and a comparison made of experimentally determined properties with literature values (*3*). Material used in this work is from the same batches prepared there.

## RESULTS AND DISCUSSION

Table I lists in columns 4, 6, and 8 the measured properties for both the mixtures and the individual components, and in other columns several quantities calculated therefrom. While $C_{18}Cl$ is in the metastable state of the supercooled liquid at this temperature, this fact is irrelevant to the work.

The density in column 4 for the $C_4Cl$-$C_{18}Cl$ system may be expressed as $d = 0.88095\,\phi_{C_4Cl} + 0.85968\,\phi_{C_{18}Cl} + \phi_{C_4Cl}\phi_{C_{18}Cl}\,[0.00058 - 0.00144\,(\phi_{C_{18}Cl} - \phi_{C_4Cl})]$, where $\phi$ represents the volume fraction of the indicated component. In this, and in other data-fitting equations below, a least-squares procedure (*8*) with a digital computer was used. The standard error in fitting density in the indicated system is ±0.00004 gram per ml. The densities show that there is a transition from expansion to contraction upon mixing in this system as $\phi_{C_4Cl}$ increases. The effect is not large, however, as may more clearly be shown by expressing the behavior in terms of the excess molar volumes, $\Delta V^E = V - (x_i V_i + x_j V_j)$. The excess molar volumes in column 5 may be expressed as $\Delta V^E = x_{C_4Cl}\, x_{C_{18}Cl}\,[0.050 + 0.237\,(x_{C_{18}Cl} - x_{C_4Cl}) - 0.351\,(x_{C_{18}Cl} - x_{C_4Cl})^2]$. Thus the departure

Table I. Properties of Systems 1-Chlorobutane–1-Chlorooctadecane and 1-Chlorobutane–1-Chlorohexane at 25° C.

| 1-Chlorobutane Mole fraction | 1-Chlorobutane Volume fraction | 1-Chlorobutane Weight fraction | Density, G./Ml. | $\Delta V^E$, Ml./Mole | Kinematic Viscosity, Cs. | $\Delta^*G^E$, Cal./Mole | Refractive Index, $n_D$ | Refractivity Intercept, $n_D - 0.5d$ |
|---|---|---|---|---|---|---|---|---|
| | | | 1-Chlorobutane-1-Chlorooctadecane | | | | | |
| 1 | 1 | 1 | 0.88095 | | 0.4837 | | 1.39996 | 0.95948 |
| 0.8563 | 0.6507 | 0.6562 | 0.87372 | −0.032 | 1.042 | 270.2 | 1.41763 | 0.98077 |
| 0.7076 | 0.4308 | 0.4367 | 0.86900 | −0.031 | 1.837 | 381.0 | 1.42869 | 0.99419 |
| 0.5426 | 0.2706 | 0.2754 | 0.86536 | 0.018 | 2.978 | 390.7 | 1.43688 | 1.00420 |
| 0.4484 | 0.2026 | 0.2066 | 0.86395 | 0.011 | 3.764 | 362.5 | 1.44027 | 1.00829 |
| 0.3173 | 0.1269 | 0.1296 | 0.86232 | 0.018 | 4.978 | 287.7 | 1.44410 | 1.01294 |
| 0.1949 | 0.0704 | 0.0720 | 0.86114 | 0.012 | 6.272 | 193.2 | 1.44700 | 1.01643 |
| 0 | 0 | 0 | 0.85968 | | 8.590 | | 1.45062 | 1.02078 |
| | | | 1-Chlorobutane–1-Chlorohexane | | | | | |
| 1 | 1 | 1 | 0.88095 | | 0.4837 | | 1.39996 | 0.95948 |
| 0.8446 | 0.8053 | 0.8066 | | | 0.5315 | 13.0 | | |
| 0.7000 | 0.6397 | 0.6417 | | | 0.5741 | 17.7 | | |
| 0.5707 | 0.5028 | 0.5050 | | | 0.6131 | 19.1 | | |
| 0.4377 | 0.3720 | 0.3740 | | | 0.6547 | 18.8 | | |
| 0.3126 | 0.2571 | 0.2587 | | | 0.6946 | 16.3 | | |
| 0.1407 | 0.1108 | 0.1117 | | | 0.7511 | 10.0 | | |
| 0 | 0 | 0 | 0.87338 | | 0.7952 | | 1.41762 | 0.98093 |

from ideal volume is about 0.03 ml. per mole at most. In the last equation the standard error is ±0.008 ml. per mole.

Densities were not measured in the $C_4Cl$-$C_6Cl$ system. From results in the $C_4Cl$-$C_{18}Cl$ system, it follows from well known effects of chain length in a homologous series that departure from ideal volume in $C_4Cl$-$C_6Cl$ mixtures should not be measurable with the apparatus used.

Volumetric behavior here may be compared with that found in *n*-alkane–*n*-alkane and *n*-alkane–1-chloroalkane mixtures. Thus at near-equimolarity, in the system *n*-hexadecane–*n*-hexane $\Delta V^E = -0.6$ ml. per mole (*9*), while it is +0.4 ml. per mole for *n*-hexadecane–1-chlorohexane (*11*). Opposing volumetric effects due to differing chain lengths and polar *vs.* nonpolar structures are evident.

Although the viscosity of a mixture is not a simple function of composition, the excess molar Gibbs free energy of activation for flow may be calculated (*4*) through the Eyring viscosity equation (*7*), $\Delta^*G = RT \ln (\nu M/hN)$, as $\Delta^*G^E = RT (\ln \nu M - x_i \ln \nu_i M_i - x_j \ln \nu_j M_j)$ through the definition $\Delta^*G^E = \Delta^*G - (x_i\Delta^*G_i + x_j\Delta^*G_j)$. The $\Delta^*G^E$ values listed in column 7 show that both systems exhibit viscosity greater than ideal. They may be expressed as $\Delta^*G^E = x_{C_{18}Cl}x_{C_4Cl} [1520.9 - 605.9 (x_{C_{18}Cl} - x_{C_4Cl}) + 327.7 (x_{C_{18}Cl} - x_{C_4Cl})^2 - 203.0 (x_{C_{18}Cl} - x_{C_4Cl})^3]$ and $\Delta^*G^E = x_{C_6Cl}x_{C_4Cl} [79.4 - 11.2 (x_{C_6Cl} - x_{C_4Cl})]$ with standard errors of ±0.8 and 1.0 cal. per mole, respectively. The nonzero $\Delta^*G^E$ values are similar to those found by Coursey and Heric in systems of *n*-hexadecane with normal chloroalkanes (*3*), where the behavior was ascribed to the difference in flow mechanisms between the shorter and longer chains.

The absence of volumetric effects in viscous behavior here offers an unusual opportunity to consider the role of the former in rendering inaccurate some equations for predicting viscosity of mixtures. These include equations which assume mole fraction additivity in $1/\eta_i$ (*1*), $\ln \eta_i$ (*12*), and $\ln \nu_i$ (*5*). For the system $C_4Cl$-$C_{18}Cl$ the standard errors by these equations are, respectively, 66.0, 33.2, and 33.6%, and they are 4.2, 1.8, and 2.0% for the system $C_4Cl$-$C_6Cl$. Every mixture viscosity predicted with these equations in these systems is less than the experimental value. The contrast in errors for each equation between the two systems clearly shows that volumetric behavior cannot be the cause of their failure to apply to the system $C_4Cl$-$C_{18}Cl$. Rather, it is the assumed additivity in mole fraction which fails.

Refractive indices in column 8 for the system $C_4Cl$-$C_{18}Cl$ may be expressed as $n_D = 1.39996\ \phi_{C_4Cl} + 1.45062\ \phi_{C_{18}Cl} - 0.00033\ \phi_{C_4Cl}\phi_{C_{18}Cl}$ with a standard error of ±0.00004. The departure from ideal refractometric behavior is, therefore, small, as is commonly found when the excess volume of mixing is small. Refractometric behavior in the system $C_4Cl$-$C_6Cl$ may be assumed to be essentially ideal, and it was not observed experimentally.

Refractometric and volumetric data may be combined to yield the refractivity intercept, which is a useful function for the correlation of these two properties (*15*). Kurtz and coworkers (*13, 17*) have shown that for various hydrocarbon homolog series the refractivity intercept is essentially constant in each series, while Thompson and coworkers have applied the property to mixtures involving other species, including polyamines (*15*), alcohols (*2*), and amino alcohols (*16*).

Kurtz and Ward (*14*) defined the refractivity intercept through the linear $n_D$ *vs.* d behavior of hydrocarbon homologs, $n_D = a + b$d, where a value of $b = 0.5$ is representative of group behavior. Thus $n_D - 0.5$d is the refractivity intercept, and this definition has been applied as such to other species. For the system $C_4Cl$-$C_{18}Cl$, the refractivity intercepts in column 9 may be expressed as $n_D - 0.5\text{d} = 0.95948\ \phi_{C_4Cl} + 1.02078\ \phi_{C_{18}Cl} - 0.00050\ \phi_{C_4Cl}\phi_{C_{18}Cl}$ with a standard error of ±0.00006.

The refractivity intercepts of the extreme 1-chloroalkanes here differ significantly, much more than is found in homologous series of hydrocarbons (*17*). This is not surprising, however, as the definition of the refractivity intercept is based upon hydrocarbon behavior. The question arises whether in the present systems a function similar to the refractivity intercept, but based upon behavior specifically within these homologs, might be independent of chain length. A least-squares fit of $n_D$ *vs.* d for the 1-chloroalkanes from 4 through 40 carbons at 25° C. (*6*) yields $n_D = 3.6102 - 2.5089$d with a maximum and standard error of 0.0001 in $n_D$. The errors are randomly distributed with chain length. Thus the 1-chloroalkanes exhibit a correlation between $n_D$ and d.

$n_D + 2.5089$d may be called a pseudo-intercept in that it has the same intended significance as the refractivity intercept, but is distinct from the later defined quantity. The data show that in the system $C_4Cl$-$C_{18}Cl$ the pseudo-intercept is not independent of the average chain length of the mixtures, and is not a more suitable function than the refractivity intercept.

## NOMENCLATURE

d = density, g. per ml.
$\Delta^*G$ = molar Gibbs free energy of activation for flow, cal. per mole
$\Delta^*G^E$ = excess molar Gibbs free energy of activation for flow, cal. per mole
$h$ = Planck constant, erg. sec.
$M$ = molecular weight, g.
$N$ = Avogadro number
$R$ = gas constant, cal. per deg. mole
$T$ = absolute temperature, deg. Kelvin
$V$ = molar volume, ml. per mole
$\Delta V^E$ = excess molar volume, ml. per mole
$n_D$ = refractive index, Na $D$ line
$x$ = mole fraction
$\eta$ = dynamic viscosity, cp.
$\nu$ = kinematic viscosity—i.e., dynamic viscosity/density, cs.
$\phi$ = volume fraction

### Subscripts

$i, j$ = generalized components

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Received for review September 19, 1969. Accepted March 2, 1970. Work supported by the Petroleum Research Fund administered by the American Chemical Society.