θ = vapor phase nonideality correction factor
β = gas-phase second virial coefficient
γ = activity coefficient
$\bar{\Lambda}$ = total pressure of system, mm. of Hg
Λ_{12}, Λ_{21} = Wilson constants

Subscripts

1 = more volatile component
2 = less volatile component
c = calculated value
i = component i

LITERATURE CITED

(1) Antoine, C., *Compt. Rend.* **107**, 681 (1888).
(2) Carlson, H.C., Colburn, A.P., *Ind. Eng. Chem.* **50**, 403 (1958).
(3) Chao, K.C., Hougen, O.A., *Chem. Eng. Sci.* **7**, 246 (1958).
(4) Herington, E.F.G., *J. Inst. Petrol.* **37**, 457 (1951).
(5) Horsley, L.H., *Advan. Chem. Ser.* No. **6**, 48-9 (1952).
(6) Jordan, T.E., "Vapor Pressure of Organic Compounds," p. 128, Interscience, New York, 1954.
(7) Lange, N.A., Ed., "Handbook of Chemistry," 9th ed., pp. 384, 1424, 1550, McGraw-Hill, New York, 1956.
(8) Lodl, S.J., Scheller, W.A., J. CHEM. ENG. DATA **12**, 485 (1967).
(9) Marek, J., *Collect. Czech. Chem. Commun.* **20**, 1490 (1955).
(10) Marek, J., Standart, G., *Ibid.*, **19**, 1074 (1954).
(11) Miller, D.G., *Ind. Eng. Chem.* **56**(3), 46 (1964).
(12) Miller, D.G., *J. Phys. Chem.* **69**, 3209 (1965).
(13) Norrish, R.S., Twigg, G.H., *Ind. Eng. Chem.* **46**, 201 (1954).
(14) Orye, R.V., Prausnitz, J.M., *Ibid.*, **57** 18 (1965).
(15) Othmer, D.F., *Ibid.*, **35**, 614 (1943).
(16) Pitzer, K.S., Curl, R.F., *J. Amer. Chem. Soc.* **79**, 2369 (1957).
(17) Raju, B.N., Ranganathan, R., Rao, M.N., *Indian Chem. Eng.* (2), T33 (1965).
(18) Redlich, O., Kister, A.T., *Ind. Eng. Chem.* **40**, 345 (1948).
(19) Reid, R.C., Sherwood, T.K., "Properties of Gases and Liquids," 2nd ed., pp. 124, 574, McGraw-Hill, New York, 1966.
(20) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Vol. II, pp. 101, 113, 277, Elsevier, Amsterdam, 1965.
(21) Vilim, O., Hala, E., Pick, J., Fried, V., *Chem. Listy* **48**, 989 (1954).
(22) Watson, K.M., *Ind. Eng. Chem.* **35**, 398 (1943).
(23) Yen, L.C., Woods, S.S., *A.I.Ch.E. J.* **12**(1), 95 (1966).

RECEIVED for review May 10, 1969. Accepted June 3, 1970.

Thermodynamic Properties of Acetone, Dimethyl Sulfoxide, and Their Solutions by Rayleigh Light Scattering

LINDA L. HAYNES, RAYMOND L. SCHMIDT, and H. LAWRENCE CLEVER
Department of Chemistry, Emory University, Atlanta, Ga. 30322

The Rayleigh light-scattering technique was applied to acetone, dimethyl sulfoxide, and their solutions to obtain isothermal compressibilities of the pure liquids and activity coefficients and excess Gibbs free energy of mixing of the solutions. The acetone–dimethyl sulfoxide solutions show an unsymmetrical excess free energy with a maximum of about 150 cal. per mole at 0.6 mole fraction acetone at 30° C. The light scattering of the pure liquids gives evidence that dimethyl sulfoxide has a temperature-dependent structuring while acetone does not. Solution densities were measured and excess volumes of mixing were found to be unsymmetrical and negative with a minimum of –0.47 ml. per mole at 0.65 mole fraction acetone.

Acetone, $(CH_3)_2CO$, and dimethyl sulfoxide $(CH_3)_2SO$, although showing superficial similarities, are different in structure, physical properties, and intermolecular forces. Acetone is a planar molecule; dimethyl sulfoxide is a pyrimidal molecule with a pair of unshared electrons on the sulfur. Some of their physical properties are compared in Table I, which leads to the expectation that their solutions will be nonideal.

Acetone–dimethyl sulfoxide solutions appear well suited for study by Rayleigh light scattering, which can be analyzed to obtain activity coefficients and excess Gibbs free energy of mixing (*5, 18*) when solution components differ in refractive index by 0.1 unit or more and the solutions show positive excess free energy of mixing. In addition, the Rayleigh scattering from pure liquids can be analyzed to obtain approximate isothermal compressibilities of the liquid (*17*) and evidence of temperature-dependent liquid structuring (*19, 20*). A recent book (*11*) gives the background and more detail about the light scattering technique.

Table I. Some Physical Properties of Acetone and Dimethyl Sulfoxide

Property	Acetone		Dimethyl Sulfoxide	
Melting point, ° C.	–95.35	(*8*)	18.52	(*3*)
Normal boiling point, ° C.	56.2	(*8*)	189	(*8*)
Molar volume, ml. mole^{-1}, 30°	74.53		71.61	
Dipole moment, *D*	2.88	(*14*)	3.9	(*4*)
Refractive index, n_D^{20}	1.3588	(*8*)	1.4783	(*16*)
Heat of fusion, cal. mole^{-1}	1366	(*10*)	3434	(*3*)
Heat capacity, liquid, cal. deg.$^{-1}$ mole^{-1}, 25°	29.8	(*10*)	36.6	(*3*)
Solubility parameter	9.9	(*9*)	12.9	(*7*)[a]
Isothermal compressibility, cm^2. dyne^{-1} × 10^{12}, 30°	152		68	
Surface tension, dyne cm.$^{-1}$, 30°	22.42	(*2*)	42.41	(*2*)

[a] Calculated from heat of vaporization calculated from vapor pressure equation of (*7*).

Table II. Rayleigh Scattering, Depolarization, and Isothermal Compressibility of Acetone and of Dimethyl Sulfoxide

Temp., ° C.	436 Mμ $R(90) \times 10^6$, cm.$^{-1}$	436 Mμ ρ_u	546 Mμ $R(90) \times 10^6$, cm.$^{-1}$	546 Mμ ρ_u	Compressibility, K_T, Cm.^{2} Dyne^{-1} × 10^{12}
			Acetone		
30.1	13.42(13.3)^a	0.165 ± 0.012(0.16)^a	4.63(5.5)^a	0.145 ± 0.012(0.16)^a	152
35.1	13.89	0.165 ± 0.014	4.73	0.145 ± 0.011	156
39.2	14.06(13.7)^a	0.150 ± 0.013(0.14)^a	4.76(5.5)^a	0.140 ± 0.016(0.15)^a	163
44.1	14.54	0.145 ± 0.015	4.95	0.120 ± 0.012	173
48.8	14.98	0.130 ± 0.015	5.09	0.125 ± 0.015	182
			Dimethyl Sulfoxide		
30.0	...	...	6.10	0.220	68
35.0	...	...	6.34	0.185	77
39.7	...	...	6.39	0.175	79
48.0	...	...	6.33	0.165	80

^{a} From values relative to benzene (*20*) and converted to acetone values using benzene data for (*17*).

EXPERIMENTAL

Materials. Acetone, Fisher, was dried over K_2CO_3 and distilled just prior to use. Dimethyl sulfoxide, J. T. Baker, was fractionally crystallized three times just prior to use. Solutions were prepared by weight in special weighing bottles (*1*) and corrections for vapor phase losses were made.

Light Scattering. A Brice-Phoenix series 2000 Universal light-scattering photometer was used to measure the total intensity Rayleigh scattering and the depolarization of the pure liquids and the solutions at 546 mμ. Measurements were not made at the 436-mμ wavelength because of a slight fluorescence in the dimethyl sulfoxide.

The data were treated as described in earlier papers (*17, 18*). The isotropic scattering contribution was separated from the total scattering by the Cabannes relation. The density fluctuation and density-concentration crossterm fluctuation were calculated and subtracted from the isotropic scattering to obtain the concentration fluctuation contribution. A function of the ideal and the solution concentration fluctuation terms was integrated to obtain the activity coefficients.

The benzene-methanol system has been used as a test system for the method. The agreement between excess free energies of mixing from the light-scattering measurements and from vapor pressure measurements is better than 3% (*18*). However, uncertainties in the measurement can be as high as 15%.

Density. Solution densities were determined in 15-ml. pycnometers with graduated constant 1.00-mm. bore neck. Temperature for the density measurement was controlled at 30.00° ± 0.01° C.

RESULTS AND DISCUSSION

Rayleigh scattering, depolarization, and isothermal compressibilities of acetone and dimethyl sulfoxide between 30° and 50° C. are given in Table II. The acetone scattering and depolarization values compare satisfactorily with values reported earlier (*20*). The acetone isothermal compressibilities are 8 to 11% higher than published results obtained by conventional methods (*15, 21*). No literature values of these properties were found for dimethyl sulfoxide.

The isothermal compressibilities from light scattering, which are atmospheric pressure values, are subject to errors from the measurement of depolarization and in the approximation of the optical dielectric constant by the Clausius-Mosotti equation which could result in a maximum error of 10%. However, in our experience with some 10 liquids (*17*) the error range in isothermal compressibility was normally 0.5 to 5%. Isothermal compressibilities are conventionally obtained from the volume change of the liquid on compression. The measurement is often made at high pressure and the compressibility at atmospheric pressure found by extrapolation over a large pressure range. This is the case for only one value of the acetone compressibility (*15*) compared above.

Shakhparonov (*19, 20*) has developed an equation for the calculation of the molecular anisotropy, γ^2, from light-scattering data. The theory suggests that a temperature-dependent molecular anisotropy is evidence of a temperature-dependent structuring in the liquid. The calculated molecular anisotropy of acetone remained constant over the 30° to 50° C. temperature range at values of 2.33 ± 0.06×10^{-48} cm.^{6} at 436 mμ and 2.47 ± 0.08×10^{-48} cm.^{6} at 546 mμ. These values compare satisfactorily with a reported molecular anisotropy for acetone of 2.7×10^{-48} cm.^{6} (*20*). The molecular anisotropy of dimethyl sulfoxide shows a regular decrease from 2.95×10^{-48} at 30° to 2.47×10^{-48} cm.^{6} at 48°, which indicates a temperature-dependent structuring in the liquid state. Independent evidence of a temperature-dependent liquid structuring in dimethyl sulfoxide comes from the freezing points of dilute solutions of dimethyl sulfoxide in benzene and in water and the relatively high entropy of fusion of dimethyl sulfoxide which have been taken to indicate the persistence of a chain-like structure from the solid into the liquid state (*12, 13*).

The Rayleigh scattering, depolarization, density, and excess volume of acetone–dimethyl sulfoxide solutions are given in Table III. In our earlier work (*2*), solution composi-

Table III. Rayleigh Scattering, Depolarization, Density, and Excess Volume for Acetone (1)–Dimethyl Sulfoxide (2) Solutions, at 30° C.

Mole Fraction, X_1	546 Mμ $R(90) \times 10^6$, cm.$^{-1}$	546 Mμ ρ_u	$1 - R_{id}/R_c$	Density, G. Ml.$^{-1}$	Excess Volume, Ml. Mole^{-1}
0.000	6.10	0.220	0.000	1.0913^a	0.00
0.2870	7.53	0.180	0.257	1.0029	−0.27
0.3869	...	...	...	0.9723	−0.36
0.4860	...	...	...	0.9421	−0.42
0.5981	7.47	0.120	0.378	...	...
0.7360	9.02	0.075	0.627	0.8649	−0.48
0.8723	7.65	0.085	0.665	0.8202	−0.22
0.9179	6.79	0.100	0.687	0.8058	−0.17
0.9423	6.79	0.115	0.693	0.7978	−0.11
1.0000	4.63	0.145	0.000	0.7793^a	0.00

^{a} Values from (*2*).

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, ΔG^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°, and solubility parameter, δ, from Table I, mole fraction, X, and volume fraction, ϕ. 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.

LITERATURE CITED

(1) Battino, R., *J. Phys. Chem.* **70**, 3408 (1966).
(2) Clever, H.L., Snead, C.C., *Ibid.*, **67**, 918 (1963).
(3) Clever, H.L., Westrum, E.F., Jr., *Ibid.*, **74**, 1309 (1970).
(4) Cotton, F.A., Francis, R., *J. Amer. Chem. Soc.* **82**, 2986 (1960).
(5) Coumou, D.J., Mackor, E.L., *Trans. Faraday Soc.* **60**, 1726 (1964).
(6) Fenby, D.V., private communication.
(7) Douglas, T.B., *J. Amer. Chem. Soc.* **70**, 2001 (1948).
(8) "Handbook of Chemistry and Physics," C.D. Hodgman, Ed., p. C-505, Chemical Rubber Publishing Co., Cleveland, Ohio, 1966.
(9) Hildebrand, J.H., Scott, R.L., "Solubility of Nonelectrolytes," pp. 243, 283, Reinhold, New York, 1950.
(10) Kelley, K.K., *J. Amer. Chem. Soc.* **51**, 1145 (1929).
(11) Kerker, M., "Scattering of Light and Other Electromagnetic Radiation," Chap. 9 and 10, Academic Press, New York, 1969.
(12) Lindberg, J.J., Kenttamaa, J., *Suom. Kemistilehti* **B33**, 98 (1961).
(13) Lindberg, J.J., Kenttamaa, J., Nissema, A., *Ibid.*, **B34**, 98 (1961).
(14) Maryott, A.A., Buckley, F., *Natl. Bur. Standards, Circ.* **537**, 18 (1953).
(15) Newitt, D.M., Weale, K.E., *J. Chem. Soc.* **1951**, 3092.
(16) Schlafer, H.L., Schaffernicht, W., *Angew. Chem.* **72**, 618 (1960).
(17) Schmidt, R.L., *J. Colloid Interface Sci.* **27**, 516 (1968).
(18) Schmidt, R.L., Clever, H.L., *J. Phys. Chem.* **72**, 1529 (1968).
(19) Shakhparonov, M.I., *Dokl. Akad. Nauk SSSR* **136**, 1162 (1961).
(20) Shakhparonov, M.I., Beke, D., *Opt. Spectry. (USSR)* **17**, 208 (1964).
(21) Staveley, L.A.K., Tupman, W.I., Hart, K.R., *Trans. Faraday Soc.* **51**, 323 (1955).

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.

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

E. L. HERIC and B. M. COURSEY
Department of Chemistry, University of Georgia, Athens, Ga. 30601

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