SOLUTIONS FORMED FROM MIXTURES OF LARGE AND SMALL GLOBULAR MOLECULES

by

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ABSTRACT

Experiments on the properties of liquid mixtures have tended to concentrate on mixtures of globular molecules of approximately equal size or on monomer - polymer mixtures. By contrast there is lack of experimental data for mixtures of large and small globular molecules. It has become more evident that data on these type of systems are essential for testing the various theoretical equations and giving stimulus to new theoretical approaches.

Octamethylcyclotetrasiloxane, $(CH_3)_8Si_4O_4$, designated throughout this thesis by OMCTS, was chosen as the large molecule because of its approximately spherical shape and its large molar volume of 312 cc. at 25°C. Activity coefficients, mutual diffusion coefficients, viscosities and excess volumes for the two systems OMCTS - benzene and OMCTS - carbon tetrachloride have been measured.

Activity coefficients were measured at 25°, 35°, 45°, 55° and 60°C by a precision static vapour pressure method. For the system OMCTS - benzene the log of the activity coefficient of the volatile component was found to vary linearly with the reciprocal of the absolute temperature, indicating that both the excess enthalpy and excess entropy were independent of temperature. Moreover for this system the excess volume is virtually zero, so that the controversial correction for expansion was negligible. Plots of the above type for the system OMCTS - carbon tetrachloride were not so conclusive because

of the smaller variation of activity coefficients with temperature. The higher temperature data has been analysed and the excess functions (entropy and enthalpy) were found to be almost temperature independent in the range 45° to 60°C. This system is complicated by the fact that the excess volume is relatively large and negative.

The magnitude of the excess enthalpy could not be predicted by any theory. The variation of the excess enthalpy and, in particular, the partial molar excess enthalpy of the volatile component with concentration was best described by equations based on volume fraction statistics such as the Hildebrand-Scatchard equation.

For both systems the excess entropy at constant volume was not zero as required by regular solution theory. Of the simpler theories the Flory-Huggins volume fraction statistics equation gave the best prediction. A more complicated equation based on scaled particle theory was found to predict the variation of the excess entropy with concentration with a surprising degree of accuracy. This scaled particle theory assumes that molecules occupy a volume proportional to their molar volumes but possess a hard core and the presence of this core causes a perturbation to the volume fraction statistics equation for the excess entropy.

Mutual diffusion coefficients were measured with a Gouy diffusiometer at 18°, 25°, 35° and 45°C. Viscosities of the mixtures were measured over the same temperature range with an Ostwald viscometer. The Gordon and Hartley-Crank equations predicted the mutual diffusion coefficients to within 8% of the experimental results in the middle of the concentration range. This agreement must be considered as most unsatisfactory as the diffusion coefficients did not change by more than ± 10% over the entire concentration range.

Bearman's prediction concerning the relationship between molar volumes, viscosities and diffusion coefficients was found to hold for the system OMCTS - benzene but not for the system OMCTS - carbon tetrachloride. The variation of mutual diffusion coefficients with temperature was adequately described by the Stokes-Einstein equation.

More refined theories of diffusion are now needed. The statistical mechanical approach by Bearman and Rice appears to be most promising but before much progress can be made it will be necessary to have an adequate theory for the equilibrium properties of solutions.

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GLOSSARY

A	Helmholtz free energy
A	surface area fraction
B	virial coefficient
D	diffusion coefficient
$\bar{D}$	diaphragm cell integral diffusion coefficient
G	Gibbs free energy
H	enthalpy
J	fringe number
M	molecular weight
P	atmospheric pressure
R	gas constant
S	entropy
T	temp (°K)
U	energy
V	molar volume
a	hard sphere diameter
b	optical level arm
c	concentration (moles/litre)
f	activity coefficient
e	2.7183
g	acceleration due to gravity
m	mass
n	number of moles
p	partial pressure
t	temp (°C)
v	volume of pyknometer
w	weight
x	mole fraction
y	hard sphere parameter
α	coefficient of thermal expansion
β	compressibility
β	diaphragm cell constant
δ	solubility parameter
Δ	density deviation

Superscripts

E	excess function
m	mixing function
$-$	partial molar quantity
o	pure component
o	diffusion - refers to pure 2
1	diffusion - refers to pure 1
$*$	tracer value

Subscripts

1	component 1 - usually OMCTS
2	component 2 - usually C_6H_6 or CCl_4
v	constant volume process

Some of the above symbols have been used for other quantities, and a number of symbols have not been defined in this Glossary. These symbols have been defined in the text and, in most cases, they are identical with those used in the original references.