Correlation of the Measured Magnetic Susceptibility of Solutions of Sodium in Liquid Ammonia

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A correlation of the molal susceptibility (χ) of solutions of sodium in liquid ammonia was made to provide empirical expressions for use in analytical and experimental studies. The molal susceptibility of the sodium in these solutions is approximately piecewise linear to the logarithm of the molarity (*M*, moles per liter).

A CORRELATION of magnetic susceptibility in sodium-ammonia solutions was made by standard methods (*4*). The data obtained from the literature are plotted in Figure 1 as molal susceptibility (χ) *vs.* ln M (moles per liter), where ln is to the base *e*. Owing to the large scatter in measurements, the correlation may more precisely represent the behavior than do the data. The equation for the critical or transition molarity (M^*), defined as the intercepts of the two sets of curves in Figure 1, is dependent only on temperature, and was obtained by solving the simultaneous equations representing susceptibility above and below the critical molarity. Additionally, an equation was produced independently from a best fit for the intersection shown in Figure 1. This was done because a plot of the susceptibility at the intersection *vs.* the logarithm of the corresponding molarity appears to be a curve, whereas the solution of the simultaneous equations of the lines generating the intersections yields a straight line. The curvature is believed to be due to the large scatter of data at concentrations just below the critical molarity, which makes it difficult to establish the values of the susceptibility accurately (within ±10%) in this region.

The magnetic molal susceptibility of sodium in solution in ammonia in the concentration region below the critical molarity, as a function of M and T (° K.), can be expressed by

$$\chi = [-326 \ln M + 13.23\,(T - 300.5)] \times 10^{-6} \tag{1}$$

to an accuracy of 5% of the least squares fit. At concentrations above that of the critical molarity, the molal susceptibility is given by

$$\chi = [0.913\,T - 170] \times 10^{-6} \tag{2}$$

to an accuracy of ±10% of a least squares fit. The susceptibility value at the critical molarity (χ^*) and the critical molarity (M^*) can be expressed by the solution of the simultaneous Equations 1 and 2 as

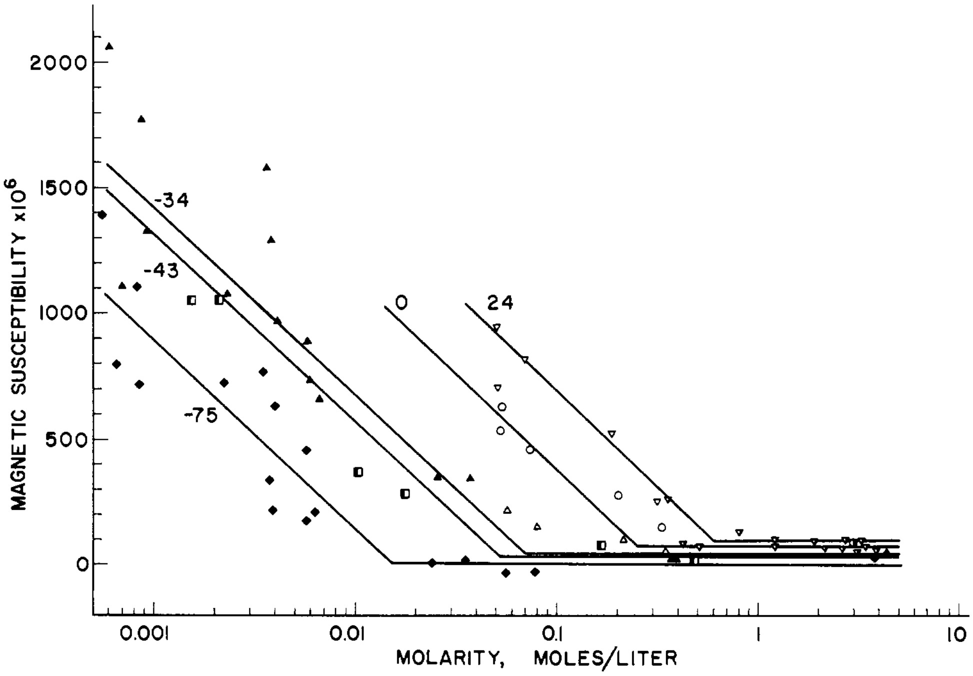

Figure 1. Molar susceptibility of sodium in sodium-ammonia solutions. Lines drawn are those calculated with Equations 1 and 2

Temperature, ° C.					
−75	−43	−34	0	24	Source
●		▲			(2)
		△	○	▽	(3)
					(1)
					(5)

$$\chi^* = [24.1 \ln M^* + 112] \times 10^{-6}$$

and

$$\ln M^* = 0.0378\ T - 11.67 \qquad (3)$$

or by a direct fit independent of Equations 1 and 2, as

$$\chi^* = \left[\frac{20}{(M^*)^{0.45}} + 130 \right] \times 10^{-6} \qquad (4)$$

These correlations were made to provide empirical relations of the susceptibility as a function of concentration and temperature. The theoretical expressions (*6*) do not, for the most part, fit the experimental data within one to two orders of magnitude.

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Vapor-Liquid Equilibrium Data for the Binary Systems Methanol-Benzene and Methyl Acetate–Methanol

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Isobaric vapor-liquid equilibrium data are presented for the binary systems methanol-benzene and methyl acetate–methanol at 1 atm. The experimental data were well correlated with the van Laar equation.

BINARY vapor-liquid equilibrium data are presented for two combinations involving methanol as one component at 1 atm. A Colburn still was used to obtain experimental data. Each set of binary data shows a positive azeotrope. The data are compared with the existing literature values.

EXPERIMENTAL

Methanol, C.P. grade, was fractionated through a laboratory glass column with McMahon packings. Benzene, C.P. grade, was purified by repeated recrystallization. Methyl acetate, C.P. grade, was refluxed with acetic anhydride and then distilled through a packed column. The distillate was shaken with anhydrous potassium carbonate and redistilled. Table I shows the experimental properties of the purified chemicals compared with literature values.

A Colburn equilibrium still was used. Boiling temperatures of mixtures were measured by a calibrated copper-constantan thermocouple and a Yokogawa P-7 potentiometer. The accuracy of temperature measurement was within ±0.05° C. Since the atmospheric pressure changed during experimental runs within a range of +1.8 and −8.2 mm. of Hg from 1 atm., observed temperatures were corrected to 1 atm. by applying the Clausius-Clapeyron equation. Compositions of binary mixtures were determined using an Atago Abbe refractometer. Refractive index reading could be done with an accuracy of ±0.0002 at 25° C.

Table I. Properties of Materials

Material	Boiling Point, ° C.		Refractive Index, 25° C.	
	Exptl.	Lit.	Exptl.	Lit.
Methyl acetate	56.8	56.8(*6*) 56.9(*13*)	1.3587	1.3589(*6*)
Methanol	64.7	64.65(*13*)	1.3263	1.3266(*14*)
Benzene	80.1	80.1(*13*)	1.4979	1.4979(*1*)

RESULTS

The liquid phase activity coefficients were calculated from the following equation of equilibrium for *i*th component

$$\varphi_i y_i P = \gamma_i x_i f_i^{0L} \qquad (1)$$

The fugacity coefficient φ_i is given by

$$\ln \varphi_i = \frac{2}{v} \sum_{j=1}^{N} y_j B_{ij} - \ln z \qquad (2)$$

The virial equation of state truncated after the second term is used to evaluate the compressibility factor z

$$z = \frac{Pv}{RT} = 1 + \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j B_{ij}/v \qquad (3)$$

The second virial coefficients B_{ii} and B_{jj} and the second virial cross coefficient $B_{ij} (i \neq j)$ were calculated from correlations based on a theory of corresponding states (*7, 8, 9*).

The liquid phase fugacity in the reference state f_i^{0L} is

$$f_i^{0L} = f_i^0 \exp\left(\frac{v_i^L P}{RT}\right) \qquad (4)$$

The reference fugacity for pure components are calculated by

$$f_i^0 = \varphi_i^s P_i^s \exp\left(-\frac{v_i^L P_i^s}{RT}\right) \qquad (5)$$

where φ_i^s is the fugacity coefficient of pure vapor i at temperature T and saturation pressure P_i^s. The three-parameter corresponding state correlation of Lyckman *et al.* (*5*) allows calculation of φ_i^s

$$\log \varphi_i^s = (\log \varphi_i^s)^0 + \omega_i (\log \varphi_i^s)^1 \qquad (6)$$

where ω_i is the acentric factor and $(\log \varphi_i^s)^0$ and $(\log \varphi_i^s)^1$ are generalized functions of reduced temperature.