Mutual Solubilities of Some Hydrocarbon Oils and Liquid Ammonia. II. Application of the Solubility Parameter Theory

By Kiyoharu ISHIDA

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The simple expression according to solubility parameter theory which has been developed by Hildebrand[1,2] and Scatchard[3] about nonpolar components, or its variant with the Flory-Huggins configurational term, has proved useful in interpreting qualitatively and often semi-quantitatively a wide variety of nonelectrolyte solutions including those of high polymers, especially when solubility phenomena are involved and when components are nonpolar. Liquid ammonia has not only a rather high dielectric constant and a dipole moment, but also hydrogen bonding capacity, although weaker than that of water or hydrogen fluoride. However, it has been observed that this theory interprets satisfactorily the solubility relationships even for the case including polar components such as water and aniline; for the systems of hydrocarbons and aniline, hydrocarbons and water, etc., values for solubility parameter of polar component, obtained from the solubility using the expression according to solubility parameter theory, are almost identical with values calculated from the vaporization energy[2]. It is interesting to study what relations are obtained for liquid ammonia systems. And also, some knowledge of the special interaction induced by polarity might be given from the differences between the theory and the experiment, which are obtained by applying the solubility data for liquid ammonia and hydrocarbon oils to the solubility parameter theory.

Expressions according to the Solubility Parameter Theory

Solubility parameter theory, which is derived under the assumption that in a mixture of two nonpolar molecules having spherical symmetry, the partial molal free energy of a component is the sum of a term from the entropy of mixing which is assumed to be ideal, and one from the heat of mixing which is derived from the London theory of dispersion forces neglecting the difference between arithmetic and geometric means, may be expressed in its simplest form as follows:

$$\boldsymbol{RT}\ln\gamma_1=V_1\varphi_2^2(\delta_1-\delta_2)^2 \tag{1a}$$

$$\boldsymbol{RT}\ln\gamma_2=V_2\varphi_1^2(\delta_1-\delta_2)^2 \tag{1b}$$

where γ_1 and γ_2 are the respective activity coefficients, V_1 and V_2 are the molal volumes of the pure components, φ_1 and φ_2 are the volume fractions, and δ_1 and δ_2 are solubility parameters defined as

$$\delta=(\varDelta E^v/V)^{1/2} \tag{2}$$

where $\varDelta E^v$ is the energy of vaporization of the pure component and V its molal volume, all at the temperature T. $\varDelta E^v/V$ is of course the "internal pressure" or "cohesive energy density". Equations (1a) and (1b) are exactly equivalent to equations of the form given by van Laar,[4] equations (3a, b) and (12).

Further complications are introduced if the effect of volume change on mixing or difference in molecular size is taken into consideration. Solutions which exhibit positive deviations from Raoult's law are formed from their constituents with an absorption of heat and volume expansion, although effect on volume change is fairly small. Effect of differences in molecular

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[1] J. H. Hildebrand, *J. Am. Chem. Soc.*, **38**, 1452 (1916); **41**, 1067 (1919); **42**, 2180 (1920); **51**, 66 (1929); **57**, 866 (1935). J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, **1**, 817 (1933).

[2] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes", 3rd. Ed., Reinhold Pub. Corp., New York, 1950.

[3] G. Scatchard, *Chem. Revs.*, **8**, 321 (1931); *Trans. Faraday Soc.*, **33**, 160 (1937).

[4] J. J. van Laar, *Z. physik. Chem.*, **72**, 723 (1910).

size upon the entropy of mixing can not be disregarded when molecular volumes are considerably different, and exhibit negative deviations from the ideal entropy ($-\boldsymbol{R}\ln x$). However, it has recently been confident[5] that since expansion of volume on mixing increases both the entropy and the enthalpy, free energy or isothermal solubility may be treated without serious error by the equations (1a, b) in which the entropy of mixing is assumed to be ideal and volume changes on mixing are neglected, despite the fact that both the actual entropy and the enthalpy are far from ideal.

When the volumes V_1 and V_2 in equations (1a, b) are replaced by empirical parameters q_1 and q_2 which may be related to the "effective volumes" of molecules of different shapes, and the term of intermolecular energy on mixing is represented by the more generalized form of D included also the contributions due to polarity instead of $\left\{\left(\frac{\Delta E_1^v}{q_1}\right)^{1/2}-\left(\frac{\Delta E_2^v}{q_2}\right)^{1/2}\right\}^2$, extensive empirical use of the van Laar equation may be possible even in the case of containing polar components, as well as nonpolar components. Then, equations (1a, b) may lead to

$$\log\gamma_1=A_{12}\Big/\left(1+\frac{x_1A_{12}}{x_2A_{21}}\right)^2 \qquad (3a)$$

$$\log\gamma_2=A_{21}\Big/\left(1+\frac{x_2A_{21}}{x_1A_{12}}\right)^2 \qquad (3b)$$

and

$$A_{12}=q_1D/2.303\,\boldsymbol{RT} \qquad (4a)$$

$$A_{21}=q_2D/2.303\,\boldsymbol{RT} \qquad (4b)$$

where x_1 and x_2 are the respective mole fractions, and A_{12} and A_{21} the van Laar constants.

Critical solution temperature, T_c, and the critical composition, x', are obtained by applying the following conditions to both components:

$$\partial a/\partial x=0, \qquad \partial^2 a/\partial x^2=0$$

where a is the activity.

When activity coefficients are expressed by Eqs. (1a, b), the followings are obtained:

$$\boldsymbol{RT}_c=\frac{2x_1'x_2'V_1^2V_2^2}{(x_1'V_1+x_2'V_2)^3}(\delta_1-\delta_2)^2 \qquad (5)$$

and at T_c,

$$x_1'=1-x_2'=\frac{(V_1^2+V_2^2-V_1V_2)^{1/2}-V_1}{V_2-V_1} \qquad (6)$$

If the molal volumes of two components are noticeably unequal and the Flory-Huggins equation[6] is applicable to the athermal mixing of liquids, and the relation of activity follows to equations of the form (7),

$$\ln\gamma_1=\ln V_1-\ln(x_1V_1+x_2V_2)+\varphi_2\left(1-\frac{V_1}{V_2}\right)+V_1\varphi_2^2D/\boldsymbol{RT} \qquad (7)$$

then, T_c and x' may be obtained from the equations (8) and (9), respectively:

$$\boldsymbol{RT}_c=\frac{2\varphi_1\varphi_2V_1V_2}{V_1\varphi_1+V_2\varphi_2}D \qquad (8)$$

and at T_c,

$$\varphi_1=\frac{V_2-(V_1V_2)^{1/2}}{V_2-V_1}, \quad x_1'=\frac{V_2^{3/2}}{V_1^{3/2}+V_2^{3/2}} \qquad (9)$$

TABLE I

COMPARISON OF D CALCULATED FROM CRITICAL DATA WITH $(\delta_1-\delta_2)^2$.

Suffix 1 and 2 represent hydrocarbon and liquid ammonia, respectively.

Component, 1	T_c,°K	Eq. (10)		$(\delta_1-\delta_2)^2$	D, Eq. (5)		obs. x_1'	Eq. (6) x_1'
		δ_1	δ_2		using obs. value for x_1'	using calcd. value by Eq. (6) for x_1'		
Toluene	265.8	9.36	13.40	16.32	16.23	15.14	0.200	0.134
Styrene	257.7	9.65	13.68	16.24	14.50	13.79	0.173	0.122
Ethylbenzene	283.9	8.93	12.70	14.21	14.92	14.07	0.173	0.119
o-Xylene	285.1	9.12	12.66	12.53	15.04	14.13	0.174	0.120
m-Xylene	287.8	8.94	12.56	13.10	15.29	14.07	0.184	0.118
p-Xylene	286.0	8.91	12.63	13.84	15.43	13.97	0.191	0.117_5
Propylbenzene	297.1	8.64	12.16	12.39	13.49	12.83	0.149	0.105
iso-Propylbenzene	293.2	8.62	12.34	13.84	13.86	12.72	0.165	0.104
Mesitylene	307.1	8.66	11.73	9.43	14.02	13.17	0.159	0.107
1-Methylnaphthalene	302.0	10.0*	11.96	3.84	13.38	13.00	0.139	0.106

* Calculated by the equation[10], $\Delta H^v_{298}=-2950+23.7\,Tb+0.020\,Tb^2$.

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[5] L. W. Reeves and J. H. Hildebrand, *J. Phys. Chem.*, **60**, 949 (1956).

[6] M. L. Huggins, *J. Chem. Phys.*, **9**, 449 (1941); P. J. Flory, ibid., **9**, 660 (1941); **10**, 51 (1942).

TABLE II

COMPARISON OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION

Suffiix 1 and 2 represent hydrocarbon and liquid ammonia, respectively

Component, 1	Temp. °C	V_1 ml./mole	δ_1 (cal./ml.)$^{1/2}$	$\frac{V_1(\delta_1-\delta_2)^2}{2.303\,RT}$	A_{12}	$\frac{V_2(\delta_1-\delta_2)^2}{2.303\,RT}$	A_{21}	$\frac{A_{12}}{A_{21}}\Big/\frac{V_1}{V_2}$
n-Hexane	20	130.6	7.42	2.36	1.991	0.50	0.782	0.544
	0	127.2	7.61	3.10	2.282	0.65	0.986	0.485
n-Heptane	20	146.5	7.54	2.52	2.244	0.48	0.773	0.553
	0	142.9	7.76	3·30	2.481	0.62	0.959	0.483
n-Octane	20	162.8	7.59	2.74	2.424	0.47	0.773	0.538
	0	159.2	7.90	3.48	2.638	0.58	0.969	0.456
n-Cetane	20	292.3	7.64[a]	4.81	3.276	0.46	0.691	0.452
2, 2, 4-Trimethylpentane	20	165.1	6.92	3.62	2.280	0.61	0.713	0.540
	0	161.5[b]	7.17	4.59	2.616	0.76	0.907	0.476
Cyclohexane	20	108.0	8.34	1.29	1.944	0.33	0.919	0.546
	0	105.5[f]	8.89	1.52	2.193	0.38	1.127	0.492
Methylcyclohexane	20	127.6	7.90	1.88	2.031	0.41	0.848	0.524
	0	124.7[b]	8.15	2.47	2.422	0.53	1.047	0.495
1-Octene	20	157.0	7.49[c]	2.75	1.968	0.49	0.605	0.579
	0	153.7[d]	7.79[c]	3.51	2.280	0.61	0.791	0.500
Cyclohexene	20	101.3	8.50[e]	1.11	1.492	0.31	0.710	0.579
	0	98.8[b]	8.84[e]	1.45	1.787	0.39	0.898	0.537
Ethylbenzene	0	119.1	9.01	1.62	1.478	0.36	0.529	0.625
o-Xylene	0	118.2	9.24	1.43	1.491	0.32	0.547	0.615
m-Xylene	0	120.3	9.09	1.57	1.532	0.35	0.565	0.601
p-Xylene[f]	0	120.7	9.04	1.62	1.511	0.36	0.549	0.608
Propylbenzene	20	139.4	8.68	1.39	1.376	0.28	0.413	0.666
	0	136.9	8.82[a]	2.03	1.767	0.40	0.566	0.609
iso-Propylbenzene	0	136.7[b]	8.75	2.10	1.697	0.41	0.550	0.602
Mesitylene	20	138.9	8.85	1.26	1.561	0.25	0.511	0.613
	0	136.5[g]	9.09[a]	1.78	1.888	0.35	0.664	0.555
1-Methylnaphthalene	20	139.4	10.05[c]	0.54	1.449	0.11	0.417	0.695
	0	137.6[g]	10.30[c]	0.88	1.725	0.17	0.528	0.633
Decalin	20	156.0[g]	7.85[h]	2.34	2.540	0.42	0.909	0.500
	0	153.4[h]	8.08[a,h]	3.13	2.670	0.54	1.079	0.430
Tetralin	20	136.1	9.50[a]	0.82	1.726	0.17	0.583	0.606
	0	133.8[i]	9.73[a]	1.24	2.053	0.25	0.711	0.576

Liquid ammonia, at 20°C, $V_2=27.90$, $\delta_2=12.34$; at 0°C, $V_2=26.67$, $\delta_2=13.13$

a) ΔH^v was estimated by extrapolation.
b) Calculated from Geist and Cannon's data[12].
c) Calculated from the equation[13], $\delta=4.1(\gamma/V^{1/3})^{0.43}$. Surface tension for 1-methylnaphthalene was estimated from parachor[19] neglecting vapor density.
d) Estimated from surface tension[14] and density at 20°C assuming that the dependency of parachor upon temperature and vapor density are negligible.
e) ΔH was estimated from vapor pressure-temperature relations according to Lister[15].
f) Values in the supercooled condition.
g) Observed value.
h) Calculated value as a mixture of 60% *cis* form and 40% *trans* form. Seyer's data[16] for density were used in calculation.
i) Estimated by extrapolation from the data in reference[17].

In equations (6) and (9) the composition at the critical solution temperature is expressed in terms of molal volumes only.

Comparison of Solubility Data with Theory

The values for the term of intermolecular energy on mixing, D, calculated from Eq. (5) using the data on the critical point for some aromatic hydrocarbons with liquid ammonia reported in Part I are shown in Table I, compared with the values obtained from heat of vaporization at each of critical solution temperature. The values of critical compositions calculated from Eq. (6) are also given in Table I, and compared with the values which are obtained graphically from the solubility data in the neighborhood of the critical solution temperature. The solubility parameter of hydrocarbons, δ_1, and

TABLE III

COMPARISON OF VAN LAAR CONSTANTS FROM MUTUAL SOLUBILITIES WITH THOSE FROM EQUATION (12)

Suffix 1 and 2 represent hydrocarbon and liquid ammonia, respectively

	Temp. °C	P[19]	ΔE^v kcal./mole	A_{12}		A_{21}	
				Eq.	obs.	Eq.	obs.
n-Heptane	20	311.3	8.34	0.325	2.244	0.110	0.773
2, 2, 4-Trimethylpentane	20	343.7	7.92	0.542	2.280	0.171	0.713
Methylcyclohexane	20	281.6	7.95	0.279	2.031	0.101	0.848
1-Octene	20	339.6[a]	8.80[b]	0.349	1.968	0.111	0.605
Cyclohexene	20	230	7.32[c]	0.188	1.492	0.078	0.710
m-Xylene	0	284.2	9.94	0.151	1.532	0.054	0.565
Propylbenzene	0	323.1	10.66	0.182	1.767	0.060	0.566
Decalin	20	369.4	9.60	0.321	2.540	0.097	0.909
Tetralin	20	335.9	12.29	0.013	1.726	0.0042	0.583
1-Methylnaphthalene	20	353.8	14.08[b]	0.002	1.449	0.0006	0.417
Liquid ammonia	20	61.1[d]	4.25				
	0	60.8[d]	4.60				

a) Estimated from surface tension[14] and liquid density neglecting vapor density.
b) Cf. Table II, c. Estimated from δ.
c) Cf. Table II, e.
d) Calculated value. Values according to King[20] were used for surface tension and densities for liquid and vapor were taken from "International Critical Tables", Vol. III, p. 235.

of liquid ammonia, δ_2, were estimated from the equation[2]

$$\delta=\left(\frac{\Delta H^v-RT}{V}\right)^{1/2} \qquad (10)$$

where ΔH^v is the heat of vaporization at temperature T. Heats of vaporization for hydrocarbons at T_c were evaluated from the slopes of the vapor pressure—temperature curves[7]. Heat of vaporization for liquid ammonia[8] and most of densities[9] used in calculating molal volumes were taken from tabulations. The critical compositions derived from the equation (6) agree with the experimental values qualitatively, but not quantitatively. However, except for two systems of mesitylene-liquid ammonia and 1-methylnaphthalene-liquid ammonia, the values for D or solubility parameter of ammonia, δ_2, calculated from Eq. (5) are, surprisingly enough, practically identical with that obtained from the heat of vaporization and the molal volume at the critical solution temperature, as in the cases of hydrocarbon-aniline system and hydrocarbon-water system. But, this agreement should be regarded as sheer good luck, owing to a compensation of disturbing factors.

As the solubility parameter of ammonia obtained from the data for the critical point is almost identical with the value calculated from the heat of vaporization as stated above, it seems that this agreement is held at other temperatures. Namely, the following equation may be written approximately;

$$D=(\delta_1-\delta_2)^2 \qquad (11)$$

In Table II, logarithms of activity coefficients at infinite dilution at the temperatures 0° and 20°C which are calculated according to equations (1a, b) or (4a, b) assumed $q=V$ and (11) are given, compared with the experimental values for the van Laar constants which are obtained from the mutual solubility data in Part I according to the equations derived by Carlson and Colburn[11]. A_{12} and A_{21} are logarithums of activity coefficients at infinite dilution of hydrocarbons in liquid ammonia-rich layer and of liquid ammonia in hydrocarbon-rich layer, respectively.

Although the experimental error and uncertainty of the numerical values for

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[7] D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

[8] "International Critical Tables", McGraw-Hill Book Company Inc., New York, 1928, Vol. V, p. 138.

[9] Ibid., Vol. III, p. 27.

[10] Cf. ref. 2, p. 427.

[11] H. C. Carlson and A. P. Colburn, *Ind. Eng. Chem.*, **34**, 581 (1942).

[12] J. M. Geist and M. R. Cannon, *Ind. Eng. Chem. Anal. Ed.*, **18**, 611 (1946).

[13] Cf. ref. 2, p. 431.

[14] J. J. Jasper and E. R. Kerr, *J. Am. Chem.* Soc., **76**, 2659 (1954).

[15] M. W. Lister, ibid., **63**, 143 (1941).

[16] W. F. Seyer and C. H. Davenport, ibid., **63**, 2425 (1941).

[17] S. Doldi, *Ann. chim. applicata*, **28**, 454 (1938); *Chem. Abst.*, **33**, 5250^5 (1939).

TABLE IV

COMPARISON OF D AND CRITICAL COMPOSITION ASSUMING DIMERIZATION OF AMMONIA WITH THOSE NOT ASSUMING DIMERIZATION

Suffix 1 and 2 represent hydrocarbon and liquid ammonia, respectively

Component, 1		Assuming $V_1=q_1$, $V_2=q_2$			Assuming $V_1=q_1$, $2V_2=q_2$				
		D	x_1'	x_1'	D		x_1'		
	$(\delta_1-\delta_2)^2$	Eq. (8)	obs.	Eq. (9)	Eq. (8)	Eq. (5)	obs.	Eq. (9)	Eq. (6)
Toluene	16.32	22.75	0.200	0.114	14.79	13.22	0.334	0.266	0.272
Styrene	16.24	21.74	0.173	0.101	13.99	12.19	0.295	0.241	0.249
Ethylbenzene	14.21	22.50	0.173	0.097	14.46	12.47	0.295	0.234	0.243
o-Xylene	12.53	22.61	0.174	0.099	14.54	12.57	0.296	0.237	0.245
m-Xylene	13.10	22.57	0.184	0.097	14.50	12.49	0.312	0.232	0.241
p-Xylene	13.84	22.48	0.191	0.096	14.43	12.41	0.320	0.231	0.240
Propylbenzene	12.39	21.97	0.149	0.083	13.98	11.53	0.260	0.203	0.215
iso-Propylbenzene	13.84	21.86	0.165	0.082	13.91	11.44	0.284	0.202	0.214
Mesitylene	9.43	22.28	0.159	0.085	14.20	11.81	0.274	0.208	0.220
1-Methylnaphthalene	3.84	22.13	0.139	0.084	14.10	11.67	0.244	0.206	0.217

TABLE V

COMPARISON OF VAN LAAR CONSTANTS ASSUMING DIMERIZATION OF AMMONIA WITH THOSE NOT ASSUMING DIMERIZATION

Component, 1	Temp. °C	Assuming NH_3				Assuming $(NH_3)_2$					
		A_{12}		A_{21}		A_{12}			A_{21}		
		Eq. (7)	obs.	Eq. (7)	obs.	obs.	Eq. (7)	Eq. (1)	obs.	Eq. (7)	Eq. (1)
n-Heptane	20	1.39	2.244	0.11	0.773	2.003	2.23	2.52	1.020	0.81	0.96
2, 2, 4-Trimethyl-pentane	20	2.26	2.280	0.20	0.713	2.045	3.24	3.62	0.956	1.04	1.22
Methylcyclohexane	20	0.98	2.031	0.09	0.848	1.787	1.68	1.88	1.099	0.71	0.82
1-Octene	20	1.28	1.968	0.09_6	0.605	1.975	2.42	2.75	0.941	0.81	0.98
Cyclohexene	20	0.53	1.492	0.06	0.710	1.282	1.02	1.11	0.943	0.55	0.61
m-Xylene	0	0.70	1.532	0.03	0.565	1.343	1.38	1.57	0.789	0.58	0.70
Propylbenzene	0	0.95	1.767	0.03_6	0.566	1.569	1.76	2.03	0.793	0.65	0.79
Decalin	20	0.30	2.540	−0.11	0.909	2.280	1.22	1.55	1.166	0.39	0.55
Tetralin	20	−0.18	1.726	−0.18	0.583	1.526	0.58	0.82	0.811	0.20	0.34
1-Methylnaphthalene	20	−0.49	1.449	−0.24	0.417	1.295	0.29	0.54	0.623	0.08	0.22

solubility parameters used in the calculation should be taken into account, values of A_{12} according to equations (1a, b), $V_1(\delta_1-\delta_2)^2/2.303\,\boldsymbol{RT}$, are generally similar to those calculated from the mutual solubility data but A_{21}'s are smaller. It may be shown from this result that the effective volumes, q's, are not exactly identical with molal volumes and they are related not only to molecular volumes, but also to their shapes and surfaces.

The semi-empirical expression proposed by Erdos[18] for calculating the constants of van Laar equations from the properties of pure components, which may be considered as a modification replaced the molal volumes in equations (1a, b) by the surface areas in terms of parachors, may be written as follows:

$$A_{12}=\frac{P_1^{2/3}}{2.303\boldsymbol{RT}}\left\{\left(\frac{\Delta E_1}{P_1^{2/3}}\right)^{1/2}-\left(\frac{\Delta E_2}{P_2^{2/3}}\right)^{1/2}\right\}^2 \tag{12}$$

where P_1 and P_2 are the parachors of the pure components 1 and 2.

The values for some representative compounds calculated from equation (12) are shown in Table III, compared with the experimental values. The ratios of effective volumes, A_{12}/A_{21}, almost agree with the experimental values, but values for each van Laar constant calculated according to equation (12) are considerably smaller than the experimental values, and the disagreement between these values is greater when compared with that obtained

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18) E. Erdös, *Chem. Listy*, **50**, 503 (1956); *Chem. Abst.* **50**, 11752 g (1956).

by equations (1a, b), or equations (4a, b) assuming $q=V$ and equation (11). It may be considered from the results shown in Table III that the effective volumes related to the difference in molecular shape or effective surface can not be expressed with only the surface areas in terms of parachors.

As the molal volumes of ammonia and hydrocarbons are considerably different, it may be impossible to expect the entropy of mixing to be ideal. The critical compositions for aromatic hydrocarbons with liquid ammonia obtained by equation (9) which is derived under the assumption that the entropy of mixing is expressed by the Flory-Huggins equation, are shown in the left half column of Table IV. Values for D which are calculated by equation (8) using the calculated values for critical compositions by equation (9) are also shown in Table IV. Calculated values for D by equation (8) are considerably greater and for compositions by equation (9) are smaller, and the disagreement is larger than the result shown in Table I, the reason being that the Flory-Huggins equation may be almost an over-correction for the size effect[5].

Ratio of van Laar constants, A_{12}/A_{21}, namely, the ratio of effective volumes corresponds to molal volume ratio in equations (1a, b), V_1/V_2. The ratios of effective volumes to those of molal volumes are given in the last column in Table II. For every case of the long chain molecule such as *n*-paraffin, the plain molecule of aromatic hydrocarbon and the semi-spherical one of *iso*-octane, values for V_1/V_2 are larger than A_{12}/A_{21}, and the ratios of the latter to the former are about 0.5 in all systems of hydrocarbon oils and liquid ammonia which have been studied. Morever, this ratio at lower temperature for a binary mixture is less than that at higher temperature; namely, it shows that effective volume for liquid ammonia derived from the solubility data is larger at lower temperature. Ratios for styrene and toluene at low temperatures, which are given in Table II, show also the same result. It will be seen from these results that though the different shape and surface of molecule may be related to the effective volume, they are not large factors for these ammonia systems, and that when V_2 is roughly doubled the ratios of molal volumes are almost similar to those of effective volumes. The change for molal volume of liquid ammonia, V_2, results in the change of mole fraction and so van Laar constants. But it may be clear that unless V_2 becomes larger, theoretical values are too far apart from the experimental.

In the case of water having strong hydrogen bonding capacity, the presence of the association states of 2, 4, and 8 molecules has been considered in addition to H_2O[21]. Also in the case of ammonia, the dimerization of ammonia has been known even in the gaseous state[22], and the molecular weight of liquid ammonia has been found to be 24.5 from the surface tension determination[20]. It is probable that a different kind of association may occur in various rates in liquid ammonia and its solution. If ammonia is assumed to form double molecules in liquid state on the average, for the sake of simplicity, the apparent mole fraction will be different from that for single molecule, but the value for solubility parameter calculated by equation (10) would be scarecely different from δ_2 used in the preceding calculations, since the dimerization of ammonia in vapor phase is almost negligible[22] and the heat of vaporization per gram is identical for both NH_3 and $(NH_3)_2$.

Values for D and for the critical composition, x', by equations (8) and (9) or (5) and (6) assuming the dimerization of ammonia are given in the right half column of Table IV, where the agreement with the experimental values is improved compared with those of the left half column calculated for the case of not assuming the association. Table V shows the comparison of the observed van Laar constants for representative compounds with values calculated from equation (7) assuming no association of ammonia and with values obtained by equations (7) and (1a, b); in both cases ammonia is assumed to form double molecules in liquid.

The result obtained by assuming the dimerization of ammonia may exhibit a far closer agreement than that the dimerization is not assumed, in view of all the approximations involved.

Summary

The result of the comparison of experimental data for the critical compositions

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and the logarithms of activity coefficients at infinite dilution for binary systems of some hydrocarbon oils and liquid ammonia with those expected from the solubility parameter theory, is that the solubility relations may be more satisfactorily interpreted by the theory by assuming that ammonia is associated nearly to dimerized form in the liquid state.

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The Chemical Research Institute of
Non-Aqueous Solutions, Tohoku
University, Katabira-cho, Sendai