

Association Numbers in Liquid Systems from Intermolecular Free Length Relationships

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The association number x in a pure liquid, mixture or solution can be obtained from $x = (L_{poly}/L_{mono})^3$ if the size of the molecules in the system is of the same order of magnitude. L_{poly} is the average free length between the associated molecular aggregates and it can be obtained from experimental values for the compressibility (ultra sonic velocity). For pure liquids L_{poly} can also be obtained from the surface tension. L_{mono} is a hypothetical free length that would prevail in the system if no association occurred and the density were unchanged. It can be obtained from the thermal expansion of the liquid. From the value for the apparent critical temperature it is also possible to calculate relative association numbers with good accuracy in homologous series. The apparent critical temperature is a hypothetical critical temperature the liquid would have if the degree of association did not change with increasing temperature. It is easily obtained from thermal expansion data. For cluster associated systems, such as those composed mainly of alcohols, organic acids and other organic compounds, the association numbers obtained are accurate within a few tenths of an association number unit. The results calculated from the three methods agree within the limits of experimental error. For the aliphatic alcohols the association numbers decrease from 3.5 for methyl alcohol to 1.3 for octyl alcohol. Formic acid and acetic acid have the values 2.2 and 2.1, respectively. For lattice associated systems, such as water and dilute aqueous solutions, the order of magnitude of association might be obtained above a certain temperature.

It is customary to divide liquids into two classes, normal and associated, which have widely different properties¹⁻³. In general associated liquids, such as water, alcohols and organic acids, have high melting and boiling points, large viscosities and high dielectric constants. They are generally miscible with one another, but the properties of the mixture are not simply related to those of the components. The explanation of these facts is that in such liquids there is a tendency for one molecule to be attached to a specific part of another. As a result of this the molecules tend to become associated into rings, chains or more complex aggregates.

Several accurate methods exist for the determination of molecular association in the gaseous phase ^{3,4}. For studies in liquid systems, and in particular pure liquids, many different methods have been suggested ⁴ but most of them yield results which are not in accord with each other, and have not been accepted for general use. In the present work some new methods will be described for studying association in both pure liquids and liquid mixtures. These methods have the advantage that the underlying principles are simple and that the results obtained from the various methods generally agree satisfactorily. The calculations are based on the employment of the concept of the free intermolecular length, which is related in a simple way to several other properties such as compressibility ⁵, surface tension ⁶, viscosity ⁷, and thermal expansion ⁸.

DEFINITIONS

The intermolecular free length in liquid systems can be defined in several ways using different molecular models ^{3,5,7,8}. When studying properties such as compressibility, surface tension and thermal expansion, which depend on molecular displacements in a direction perpendicular to the molecular surfaces, the molecules can be assumed to be spherical and having either a hexagonal or cubical packing. Under these assumptions, simple stereometric considerations give a molecular diameter

$$d = kV_0^{\frac{1}{3}} \quad (1)$$

where V_0 is the molar volume at absolute zero and $k = (2^{\frac{1}{3}}/N)^{\frac{1}{3}} = 1.329 \times 10^{-8}$ and N is Avogadro's number.

For a non-associated substance the diameter is unchanged when the temperature is raised, but the liquid expands as a whole as is illustrated in Fig. 1. The free length between the surfaces of the molecules is on the average $L_T = k(V_T^{\frac{1}{3}} - V_0^{\frac{1}{3}})$ where V_T is the molar volume at the temperature T° K.

For associated substances the free length depends on the degree of association as is illustrated in Fig. 2. If the density is constant the free length increases with increasing association. An equation describing this relationship can be obtained in the following way. The association number x is defined as the average number of monomeric molecules clustered together in the liquid. The molar volumes are x times those of the monomeric substance and the free length in the associated liquid is given by

$$L_{poly} = k(x^{\frac{1}{3}}V_T^{\frac{1}{3}} - x^{\frac{1}{3}}V_0^{\frac{1}{3}}) \quad (2)$$

Further, it is convenient to introduce the hypothetical free length L_{mono} which would prevail in the liquid (with unchanged density) if there were no association and the molecules were evenly distributed as is shown in Fig. 2. Thus

$$L_{mono} = k(V_T^{\frac{1}{3}} - V_0^{\frac{1}{3}}) \quad (3)$$

From (2) and (3) the association number can be obtained

$$x = (L_{poly}/L_{mono})^3 \quad (4)$$

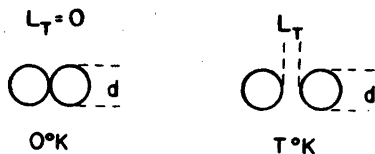


Fig. 1.

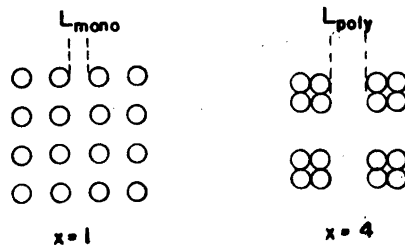


Fig. 2. Illustration of basic principle for calculation of association number x from equation (4). L_{poly} is the actual free length in the associated liquid and L_{mono} is a hypothetical free length which would prevail if the molecules were unassociated and evenly distributed.

This equation is the basic formula for determining association numbers in this work.

Another relationship sometimes useful for determining association numbers in homologous series is

$$x = (d_{poly}/d_{mono})^3 \quad (5)$$

which is obtained by an argument analogous to that used in obtaining equation (4). The actual average diameter of the associated molecules is d_{poly} , and d_{mono} is the hypothetical diameter which the molecules would have if they were unassociated.

Liquid mixtures can be treated in the same way as pure liquids utilizing free length relations if the molecular size of the two or more components is of the same order of magnitude. The molecular weight of a mixture is $M_{1,2,\dots,n} = m_1M_1 + m_2M_2 + \dots + m_nM_n$ where M_n and m_n are the molecular weight and mole fraction of the compound n .

APPARENT CRITICAL TEMPERATURE

The critical temperature for a liquid system can be obtained graphically from the ratio between the density values at two temperatures⁸. The method is applicable to both pure liquids and liquid mixtures.

For associated systems this method is of special interest for the following reasons. In order to calculate the zero point molar volume, to be used in equation (3), for an associated liquid, its reduced temperature must be known⁸. For that purpose one could not use the observed critical temperature since the critical temperature value is strongly dependent on the size of the molecular aggregates. Since the degree of association changes with temperature the observed critical temperature has no significance for predicting the thermal contraction of the liquid except near the critical point. For determining the reduced temperature at any temperature far from the critical point one should instead use an apparent critical temperature $T_{c,app}$ defined as the critical temperature the liquid would have if the degree of association did not change with increasing temperature. Since the association can be regarded as constant within small temperature ranges, such an apparent critical temperature at any temperature T can be obtained according to the

method described previously⁶. It is necessary to know the densities at two temperatures $T + \Delta T$ and $T - \Delta T$ where ΔT is about 5 to 10°. Apparent critical temperatures have been calculated for some associated liquids (Table 2). In general the apparent critical temperature is larger than the observed critical temperature. This is consistent with the fact that the degree of association is generally larger at lower temperatures.

When the apparent critical temperature is known at a certain temperature the zero point density can be obtained as well as the hypothetical free length L_{mono} at any temperature⁶. The hypothetical diameter d_{mono} can also be calculated.

EMPIRICAL FREE LENGTH RELATIONSHIPS

To arrive at L_{poly} in equation (4) or d_{poly} in equation (5) it is necessary to employ certain empirical relationships.

The adiabatic compressibility β and the surface tension σ can be related to the intermolecular free length^{6,8}. If the free length is defined as stated above and the zero point density is calculated according to the method previously described⁸ the following relations hold

$$\beta = k_{\beta} L^{2.4} \quad (6)$$

$$\sigma = k_{\sigma} L^{-1.5} \quad (7)$$

L represents either L_T in a normal liquid or L_{poly} in an associated liquid. The constants k_{β} and k_{σ} vary slightly with the temperature (Table 1). Equation (6) makes it possible to determine the free length in any liquid or liquid mixture from its adiabatic compressibility. The compressibility can be accurately obtained from experimental values for the sound velocity and the density^{10,5}. Equation (7) makes it possible to determine the free length in a pure liquid from its surface tension.

Table 1. Values for the constants k_{β} and k_{σ} in cgs-units at various temperatures.

Temp °C	0	10	20	25	30	40	50
log k_{β}	9.770	9.752	9.736	9.728	9.722	9.711	9.702
log k_{σ}	-13.530	-13.509	-13.490	-13.481	-13.472	-13.456	-13.441

It is of interest to know the accuracy of equations (6) and (7). The average deviation in free lengths, determined as previously^{5,6}, is 2.1 % for 42 normal organic liquids of various types in the case of equation (6). The corresponding deviation for equation (7) was 2.3 %. No systematic errors occur due to specific elementary compositions or from certain types of chemical constitution (Fig. 3).

The critical temperature value for a liquid depends on the molecular size and the elementary composition. For homologous series the critical temperature has been found to be a linear function of the product of the molecular diameter d and the zero point density ρ_0 (Fig. 4). In general, the relationship can be written

$$T_c = k_t \rho_0 d + l \quad (8)$$

where k_t and l have constant values for each homologous series. The relation, tested for 25 substances, holds with an average accuracy of better than 1 % in the values for the critical temperature.

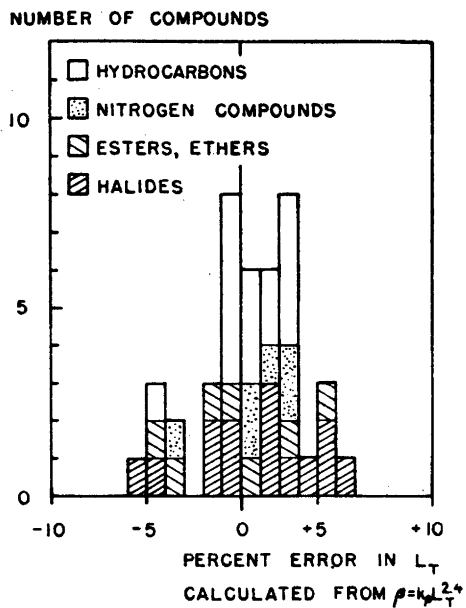


Fig. 3. Error distribution plot of equation (6) tested by 42 normal organic liquids.

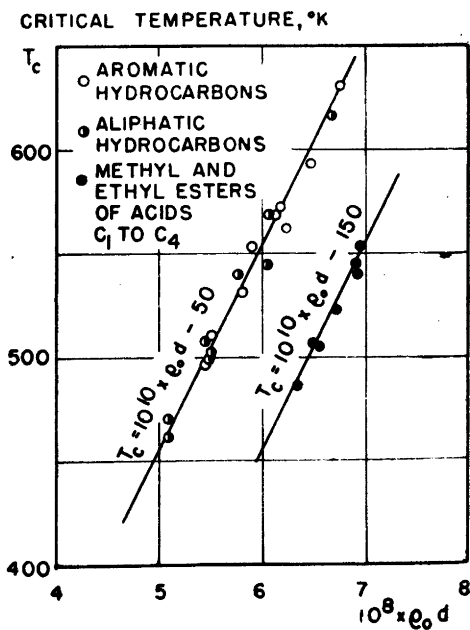


Fig. 4. For homologous series the critical temperature is a linear function of the product of the zero point density ρ_0 and the molecular diameter d .

Table 2. Association numbers (x) calculated by various methods.

Compound	Temp.	Meas- ured critical temp. ^a	Appar- ent critical temp. at $t^{\circ}b$	x calcd. from com- pressi- bility ^c	x calcd. from surface tension ^d	x calcd. from T_c, app Rela- tive accu- racy	Selec- ted value for x	Asso- ciated mole- cular weight xM
	$t^{\circ}C$	$T_c^{\circ}K$	$T_c, app^{\circ}K$			± 0.1		
Methyl alcohol	20	513.3	553	3.53	(3.01)	(3.53) ^e	3.5	112
Ethyl alcohol	0	516.3	593	2.81				
	10		590	2.77	2.76			
	20		586	2.70	2.70	2.77	2.7	124
	30		582	2.62	2.65			
	40		578	2.52	2.59			
	50		574	2.41	2.51			
<i>n</i> -Propyl alcohol	20	536.9	624	2.35	2.33	2.32	2.3	138
<i>iso</i> -Propyl alcohol	20	516.7	598	2.30	2.31	2.24	2.3	138
<i>n</i> -Butyl alcohol	20	560.2	639	1.90	1.94	1.95	2.0	148
<i>iso</i> -Butyl alcohol	20	552.3	636	2.06	2.12	1.96	2.0	148
<i>sec</i> -Butyl alcohol	20		619			1.84	1.8	133
<i>tert</i> -Butyl alcohol	20		569	1.62	1.85	1.64	1.6	119
<i>n</i> -Amyl alcohol	20		670	1.78	1.82	1.78	1.8	159
<i>active</i> Amyl alcohol	20		650			1.69	1.7	150
<i>sec</i> -Amyl alcohol	20		625		1.58	1.56	1.6	141
<i>tert</i> -Amyl alcohol	20		568		1.21	1.30	1.3	115
Diethylcarbinol	20		608		1.39	1.44	1.4	123
<i>n</i> -Hexyl alcohol	20		686	1.60	1.86	1.59	1.6	163
<i>n</i> -Octyl alcohol	20		705	1.29	1.48	(1.29) ^e	1.3	169
Ethylene glycol	20		845	2.44			2.4	149
Glycerol	20		1 030	2.45			2.5	230
Benzyl alcohol	20		749	1.31	1.34		1.3	141
Formic acid	20		608	2.25	1.96		2.2	101
Acetic acid	20	594.8	590	2.12	1.97		2.1	126
Propionic acid	20	610.8	581	1.56	1.49		1.6	119
<i>n</i> -Butyric acid	20	627.9	600	1.39	1.36		1.4	123
<i>n</i> -Valeric acid	20	652.1	624	1.28	1.26		1.3	133
Acetone	20		504	1.18	1.09		1.2	70
Methylethylketone	20		526	1.07			1.1	79
<i>cyclo</i> -Hexanone	20		636	1.48	1.45		1.5	147
Formamide	20		745	2.97	(1.81)		3.0	135
Phenylhydrazine	20		761	1.02	1.20		1.1	119
(Aniline) ^f	20		687	0.95	0.99		1.0	93
(Nitromethane) ^f	20		553	1.09	1.00		1.0	61
(Water) ^g	20	647.2	(2 000)	(225)	(73)	(60) ^h	(60)	(1 080)
	30		(1 480)	(77)	(28)	(30) ^h	(30)	(540)
	40		(1 260)	(39)	(16)	(21) ^h	(20)	(360)
	50		1 120	24	11	16 ^h	15	270
	60		990	14	7.0	13 ^h	13	234
	70		910	9.9	5.1	10 ^h	10	180
	80		850	7.2	4.0	9.1 ^h	7	126
	90		820	5.8	3.5	8.4 ^h	6	108

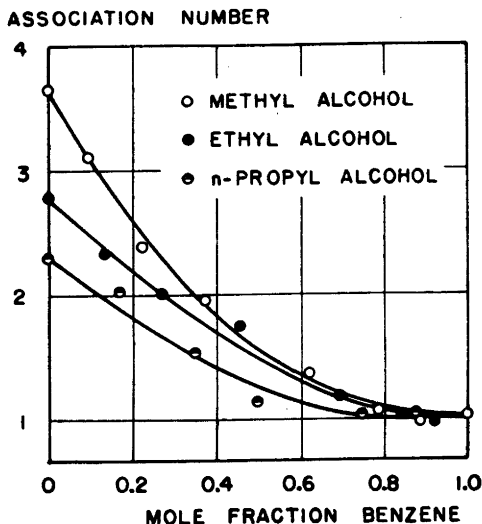


Fig. 5. Association numbers in benzene mixtures with some alcohols.

RESULTS

Utilizing values for L_{poly} determined from compressibility or surface tension data, and L_{mono} from thermal expansion data, association numbers for pure liquids can be calculated from equation (4). Some examples are given in Table 2.

Equation (8) makes it possible in certain cases to calculate relative association numbers from the apparent critical temperatures. If the association numbers are known for two compounds in an homologous series the constants in equation (8) can be evaluated and the associated molecular diameter d_{poly} can be calculated for the other compounds in the series. Since d_{mono} can be obtained from equation (1) association numbers can be calculated from equation (5). Utilizing the association numbers determined for methyl alcohol and octyl alcohol from compressibility data, the constants for aliphatic alcohols were determined to $k_1 = 1.9 \times 10^{10}$ and $l = 698$.

a Values taken from Timmermans ⁹.

b Calculated from ratio of densities at 15° and 25°, or 0° and 30°, or 15 and 30° C. Accuracy $\pm 10\%$.

c Compressibility values taken from Bergmann or Schaaffs ¹⁰. Maximum error in x estimated to ± 0.3 units or $\pm 15\%$.

d Surface tension values taken from Timmermans ⁹ and Landolt Börnstein Tabellen. Maximum error in x estimated to ± 0.3 units or $\pm 15\%$.

e Chosen value for determining constants in equation (8).

f Non-associated compound included for comparison.

g Lattice associated liquid. Values given are order of magnitude.

h Calculation made under the assumption that water is the first homologue of the alcohols.

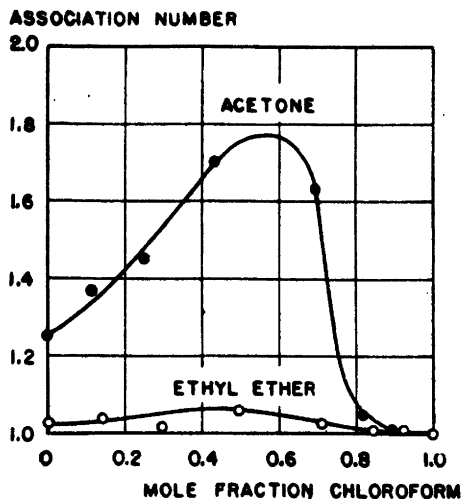


Fig. 6. Association numbers in chloroform mixtures with acetone and diethyl ether.

For liquid mixtures association numbers can be obtained from compressibility data in the same way as used for pure liquids. Ultra sonic velocity, density and thermal expansion were measured for a number of liquid systems with an experimental technique previously described¹¹. Some examples of association numbers obtained are given in Figs. 5 and 6. Due to the surface absorption as predicted by Gibbs' adsorption equation⁶ formula (7) cannot be used for calculating free lengths in the bulk of liquid mixtures. Therefore, association numbers cannot be obtained in liquid mixtures from surface tension data.

Errors in the association numbers calculated arise from three different sources. In the first place the molecular model used assumes spherical shape which is an oversimplification. This problem was investigated in a previous study⁵ and it was found unnecessary to employ any form factors for low molecular weight substances. Secondly, there are uncertainties involved in the determination of the apparent critical temperature and the zero point density⁸. Furthermore, the empirical relationships (6), (7) and (8) have certain inaccuracies as discussed above.

If the errors from different sources are added together in the most unfavourable manner the maximum error for the compressibility and the surface tension method is found to be ± 0.3 association number unit or $\pm 15\%$ whichever is the larger. The probable error is less than ± 0.2 association number unit. The apparent critical temperature method for calculating relative association numbers from equation (5) and (8) in homologous series, holds with an accuracy better than ± 0.1 association number unit.

DISCUSSION

Among associated systems one can distinguish between such cases where a true cluster association occurs, as is the case for certain organic liquids, and such cases where a quasicrystalline order prevails throughout the whole liquid, as for water. In the former case the calculation of association numbers from free length relationships is straightforward. In the latter case, which will be referred to as lattice associated systems, the calculation of association numbers does not have the same clear physical significance. The distinction between these two cases, however, is more a matter of degree than of type.

The free length method for determining association numbers seems to offer a possibility for distinguishing between the two types of association. The surface molecule in a molecular lattice does not have the same freedom to associate with its neighbouring molecules as does a bulk molecule. Therefore, it is to be expected for a lattice associated liquid that the association numbers determined from the surface tension are lower than those calculated from the compressibility. As is seen from Table 2 this is the case for water. Methyl alcohol and formamide are also slightly lattice associated which is possible in view of their chemical constitution. When the association number obtained from compressibility data agrees within the limits of experimental error with that calculated from surface tension data, the liquid is cluster associated.

For the cluster associated liquids the associated molecular weights in Table 2 lies between 70 and 230. The values are of a reasonable order of magnitude since most organic liquids have molecular weights in that range⁴. Non-associated, saturated, organic substances that contain oxygen or nitrogen generally are in the gaseous state at room temperature if their molecular weight is below approximately 65. They are generally in the solid state if the weight is larger than 250 to 300.

It is of interest to observe that for the series of homologues the association numbers decrease with increasing length of the chain. This is to be expected from the increasing paraffin character of the substances. For isomeric compounds such as butyl alcohols or amyl alcohols the association numbers decrease with increased branching of the chain. This is probably due to a steric hindrance of the association. For propionic acid and the higher carboxylic acids the apparent critical temperatures are lower, by about 5 %, than the observed critical temperatures. This anomalous behavior, if significant, would indicate that the degree of association is slightly larger at higher temperatures than at lower temperatures. Another experimental observation consistent with this conclusion is that the dielectric constant increases with increasing temperature for the carboxylic acids contrary to most other substances¹².

The results obtained for the liquid mixtures constitute a support for the correctness of the free length method for calculating association numbers. Other methods of investigation³ have shown that the association of the alcohols is hindered by the presence of benzene. The results obtained here are in accordance with these observations. In the case of acetone and chloroform a complex formation³, known from other methods, causes the association number to have a maximum at about 0.5 mole fraction. The same is true for ether-chloroform though the complex formation apparently is less pronounced.

This is probably because the oxygen atom in ether, due to steric hindrance, is less accessible for hydrogen bonding than the oxygen in acetone. The fact that pure ether is unassociated whereas acetone is slightly associated offers further evidence that this is a probable explanation for the differences observed in the two kinds of mixtures.

It should be observed that the free length method gives no information about the type of association taking place in a mixture. It only tells on the average if the mean cluster size is smaller, equal to or larger than that expected if no change of association occurs on mixing.

As stated above the concept of free length has no significance when the molecules are bound together with highly directional forces similar to those in the solid state. However, with rising temperature the lattice order is reduced and the system gets more like that of an ordinary liquid. Above some temperature, therefore, it may be possible to treat the liquid as a cluster associated system. In Table 2 the results for water have been tabulated for the temperature range 20° to 90° C. Above 50° the results from the compressibility method and the apparent critical temperature method generally agree within a factor of about 1.5. Furthermore, the associated molecular weights obtained above 50° are of a reasonable order of magnitude in view of the physical properties of water. Therefore, it appears as if the free length method could be used above that temperature to determine the order of magnitude of the association of water. At temperatures lower than 50° C quantitative results cannot be obtained for pure water or dilute aqueous solutions. Since the association in water generally is strongly reduced by the presence of other molecules, the temperature limit for qualitative studies is lowered with increasing concentration of the non-aqueous component.

The compressibility of water has a minimum at about 60° C¹⁰. The decrease between 0 and 60° is the result of a breakdown of the association so that the free length decreases in spite of the increase in specific volume. The same explanation applies to the minimum observed when the compressibility is studied as a function of increasing concentration of a liquid in mixture with water¹¹.

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