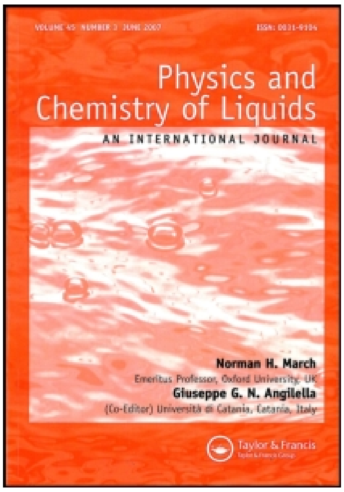

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Prediction of Equilibrium Properties of Single and Binary n-Alcohols

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A description of equilibrium quantities, including the excess functions of mixing, was possible using a small number of parameters essentially obtainable from the properties of pure components. For this purpose, molecules were divided into segments, segments related to graph points, interesting walks on graphs counted, and thermodynamic properties expressed in terms of interactions of pairs of walks. For such an approach, the association of alcohols is irrelevant and no reference to association schemes was made. "Odd" behaviour of the lower members of the homologous series of n-alcohols was discussed in terms of walks on corresponding graphs.

1. INTRODUCTION

At the present stage of liquid state theory, it appears that, in many cases, further progress is limited by our still insufficient understanding of simpler systems—consisting of spherical molecules or of mixtures of liquids belonging to the same homologous series.

We have chosen to study the thermodynamic properties of n-alcohols and their mixtures for a number of reasons. First, in the context mentioned above, the study of such systems should precede the investigation of more complicated

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ones, in this case those containing alcohols together with other components. The objects of our study, however, are not too simple; in view of the association of alcohols, current interpretations of systems involving them[1] are in fact generally based on the notion of association. The series includes a relatively large number of members in the liquid state at room temperature, where most measurements have been made. Experimental data available are fairly extensive, including determinations by Diaz Peña and Fernandez Martin[2] and careful measurements by Benson and his colleagues.[3]

Associated solutions are usually described by postulating that certain kinds of multimers are present, and by assuming values for association reaction constants, heats of association, etc., so as to reproduce the experimentally measured quantities. In the study of excess thermodynamic properties it is thus necessary to have a number of adjustable parameters accounting for the association. We shall endeavour to describe the properties of alcohols and their mixtures without the use of association parameters, in fact without any reference to association schemes. This might be possible as, whatever the association behaviour of, say, hexanol may be, it cannot be widely different from that of heptanol.

One can also expect, as no other components but alcohols are present, that intermolecular forces and the structure of mixtures should be essentially the same as those found in pure liquids. If this is the case, neither "mixed" parameters characterizing new phenomena occuring in mixtures which supposedly have not occurred in pure components, nor any combining rules should be necessary. Thus, our second objective is to describe mixtures in terms of the properties of pure components alone.

In a number of cases, the study of a property for the series of alcohols reveals "odd" behaviour in the lower members of the series, methanol and ethanol in particular, when drawing, e.g., the curve of a given property as a function of the chain length. Our further objective will be, therefore, to discuss this particular phenomenon.

2. BASIC RELATIONS

As the main variable in the series of n-alcohols is the length of the molecule, it is only natural to divide molecules into segments. We assume that there are three kinds of segments: OH groups referred to by subscript "o", middle carbon, i.e., CH_2 groups, referred to by subscript "m", and end carbon, i.e., CH_3 groups, represented by subscript "e".

We also intend to study the behaviour of longer parts of molecules, i.e., the effects of neighbouring segments upon the properties and interactions of a given segment. To do this, we assume that each segment, as defined above, corresponds to a point on a graph. An approach based on this correspondence has been proposed before.[4] For the present work, the following notions are of importance. A graph itself may be simply defined as a set of points, plus a set of lines connecting them. An alternating sequence of points and lines, beginning and ending with points, is called a walk. In view of the last definition, a segment of a molecule, i.e., a point on the respective graph, represents a walk of length $\ell = 0$. A pair of neighbouring segments considered as a single entity represents a walk of length one, a triplet of segments is a walk with $\ell = 2$, etc. The total number of walks of length ℓ in a given graph may be obtained from the adjacency matrix of the graph.[5] This number might include, particularly for long walks, some walks which for physical reasons are not interesting or just redundant; already for $\ell = 2$, we have, for example, a walk aba beginning and ending at the same point. What is needed, therefore, are number Γ_l, of equivalent classes of interesting walks[6] rather than total numbers of walks. As formulas for Γ_l, with $\ell \leqslant 5$ have been derived in the same paper,[6] we have used them directly in the present work.

To calculate equilibrium properties of a system, we consider walks of a specified length as the units interacting among themselves. We make the usual assumption of confining ourselves to binary interactions; that is, interactions of higher order are "hidden" in the binary terms. A simple algebraic argument shows[4] that contributions from single units are completely contained in the binary terms. Thus

$$F = 0.5\, \Sigma_y\, \Sigma_{y'}\, x_y x_{y'}\, F_{yy'} \tag{1}$$

where F denotes one of a number of certain thermodynamic quantities to be specified below per mole of units, x_y is a mole fraction and F_{yy^1}, is a characteristic parameter.

The parameters F_{yy^1}, of interest may be expressed in terms of pair interaction energies u(R) and pair radial distribution functions g(R), where R denotes the distance between a pair of interacting units. According to the standard relation for the configurational energy

$$U^c = 0.5\, \Sigma_y\, \Sigma_{y'}\, N_y\, N_{y'}\, V^{-1} \int u_{(yy')}(R) g_{yy'}(R)\, 4\pi R^2\, dR \tag{2}$$

where V is the volume of the system. Therefore

$$U_{yy'} = 0.5\, N^2\, \overline{u_{yy'}}\, \frac{\int g_{yy'}(R)\, 4\pi R^2\, dR}{V} \tag{3}$$

with N denoting the total number of units, and the average interaction energy $\overline{u_{yy}}$, of a unit of type y with a unit of type y′ given by

$$\overline{u_{yy'}} = \frac{\int u_{(yy')}(R) g_{yy'}(R) R^2 \, dR}{\int g_{yy'}(R) R^2 \, dR} \qquad (4)$$

The term $V^{-1} \int g_{yy'}(R) R^2 \, dR$ in Eq. (3) is retained to emphasize the fact, that beyond some distance R^o_{yy}, the contribution of a pair of units to the total value of U^C becomes negligible; assuming this term to be unity would mean assuming that a pair of units in the liquid state interacts no matter how large their separation.

To consider volume, standard "pressure equation", i.e., $P = P[u(R), g(R)]$ – cf. e.g. [7] – is necessary. If we confine our considerations to low pressures, say, $p < 1 \text{ J cm}^{-3}$, pressure becomes a small difference of two larger quantities, and we may neglect it altogether. The standard pressure equation gives

$$V = \frac{1}{6NkT} \Sigma_y \Sigma_{y'} N_y N_{y'} \int R \frac{du_{(yy')}}{dR} g_{yy'}(R) 4\pi R^2 \, dR \qquad (5)$$

where k is the Bolzmann constant and T is the thermodynamic temperature. Thus, to make Eq. (1) applicable for $F = V$ we set

$$V_{yy'} = \frac{2\pi N}{3kT} \int \frac{du_{(yy')}}{dR} R^3 g_{yy'}(R) \, dR \qquad (6)$$

It is now possible to deal with the isobaric expansivity $\alpha = V^{-1} (\partial V/\partial T)_p$, isothermal compressibility $\kappa_T = -V^{-1}(\partial V/\partial P)_T$, and adiabatic compressibility $\kappa_s = -V^{-1}(\partial V/\partial P)_s$. It is evident from the definitions that Eq. (1) is also applicable for $F = \alpha V$, $\kappa_T V$ and $\kappa_s V$, while $F \neq \alpha$, κ_T nor κ_s.

To conclude this section, let us comment briefly on the case of ideal mixtures, i.e., those obeying Raoult's law. We find, that the formalism such as proposed in (4) and discussed above gives for this specific case

$$\overline{u_{ab}} \int g_{ab}(R) R^2 \, dR$$
$$= 0.5 \left[\overline{u_{aa}} \int g_{aa}(R) R^2 \, dR + \overline{u_{bb}} \int g_{bb}(R) R^2 \, dR \right] \qquad (7)$$

where a and b denote components of the binary mixture.

3. WALKS ON MOLECULES

Let us denote the number of carbon atoms in a molecule of n-alcohol by r. Thus, according to the definitions accepted above, the number of segments or of walks of length zero in a molecule is $\Gamma_o = r + 1$. The concentrations of the units of the three kinds are respectively $x_m = (r-1)/(r+1)$ and $x_e = x_o = .(r+1)^{-1}$; this applies to a single molecule or to a pure substance. In a mixture of molecules of different lengths, one has to average r as $\Sigma_i x_i r_i$, where the index i refers to the components. In the present case, Eq. (1), (now per mole of molecules instead of per mole of segments), takes the form:

$$F = \frac{(r-1)^2}{2(r+1)} F_{mm} + \frac{1}{r+1} (0.5 F_{ee} + 0.5 F_{oo} + F_{eo}) + \frac{r-1}{r+1} (F_{me} + F_{mo})$$

$$= \frac{(r-1)^2}{2(r+1)} F_1 + \frac{1}{r+1} F_2 + \frac{r-1}{r+1} F_3 \tag{8}$$

where we have taken advantage of the fact that certain coefficients are the same and reduced the number of parameters from 6 to 3. The new symbols, F_1, F_2 and F_3 are introduced with obvious meaning.

Let us turn now to $\ell = 1$. From the segment CH_2 we now obtain in a natural way the walk $CH_2 \cdot CH_2$, from CH_3 the walk $CH_3 \cdot CH_2$ and from OH the walk $CH_2 \cdot OH$. For each molecule, the equation for Γ_1 derived in [6] gives $\Gamma_1 = r$. A new type of unit appears, however, in the methanol molecule, namely the molecule itself. Including the latter would increase the total number of characteristic parameters from 6 to 10 and would render difficult the formulating of an expression in terms of r, corresponding to Eq. (8). In fact, a separate equation for mixtures containing methanol would be necessary. We therefore exclude methanol and methanol-containing mixtures from our treatment for $\ell = 1$. Now,

$$F = \frac{(r-2)^2}{2r} F_{mm} + \frac{1}{r} (0.5 F_{ee} + 0.5 F_{oo} + F_{eo}) + \frac{r-2}{r} (F_{me} + F_{mo})$$

$$= \frac{(r-2)^2}{2r} F_1 + \frac{1}{r} F_2 + \frac{r-2}{r} F_3 \tag{9}$$

where again we have reduced the number of characteristic parameters necessary in actual calculations from 6 to 3.

Finally, let us turn to $\ell = 2$. According to the respective relation in [6], we have $\Gamma_2 = r-1$. For reasons analogous to these discussed for $\ell = 1$, we now exclude both methanol and ethanol. If this is done, we are able to write

$$F = \frac{(r-3)^2}{2(r-1)} F_{mm} + \frac{1}{r-1} (0.5 F_{ee} + 0.5 F_{oo} + F_{eo}) + \frac{r-3}{r-1} (F_{me} + F_{mo})$$

$$= \frac{(r-3)^2}{2(r-1)} F_1 + \frac{1}{r-1} F_2 + \frac{r-3}{r-1} F_3 \tag{10}$$

To test the validity of our approach, three orders of approximation seem sufficient. We therefore do not consider $\ell > 2$ but turn to computations of numerical values of thermodynamic properties.

4. CALCULATIONS AND RESULTS

Volumes: Eqs. (8-10) were applied in turn to the molar volumes of pure com-

TABLE 1

Molar volumes at 298.15K

		V, $cm^3\ mol^{-1}$		
r	Experimental	$\ell = 0$	$\ell = 1$	$\ell = 2$
1	40.73[a,b]	41.87	–	–
2	58.68[a,b]	58.69	58.68	–
3	75.16[b] 75.14[a]	75.38	75.39	75.35
4	91.96[a,b]	92.02	92.02	92.02
5	108.63[a]	108.63	108.63	108.63
6	125.26[b] 125.23[a]	125.22	125.22	125.22
7	141.96[a]	141.81	141.81	141.81
8	158.42[b] 158.39[a]	158.39	158.39	158.39
9	174.92[a]	174.97	174.97	174.95
10	191.51[a] 191.43[b]	191.54	191.54	191.52

[a] Selected values of properties of chemical compounds, Thermodynamics research center data project, Texas A and M University, College Station, Texas.

[b] Ref. 3

ponents at 298.15K, as it is at this temperature that excess volumes of binary mixtures have been measured by Benson *et al.*[3]. The results, along with reliable experimental data, are given in Table 1. The parameters obtained by an approximate computer procedure (least squares fit of an overdetermined system of equations linear in three unknowns), and used in these calculations are listed in Table 2.

The values in Table 1 show that, except for methanol, a satisfactory representation of experimental data is possible using a relation corresponding to the

TABLE 2

Pair interaction volumes at 298.15K (in cm^3, mol^{-1})

ℓ	V_1	V_2	V_3
0	33.115	83.745	75.777
1	33.130	117.368	92.234
2	33.118	150.694	108.798

general form of Eq. (1). The discrepancy for methanol is expected, from the discussion in the preceding section. As we habitually think of the volume of a system as resulting from the volumes of its constituent parts, it must be remembered that single or no-external-interaction terms now make their contributions through the binary terms; each of the binary terms contains single terms plus the binary term proper.

It is worth noting, that the parameter V_1 or V_{mm} represents interactions between methylene groups, the same as occur in n-alkanes. Indeed, comparison of parameters in Table 2 with the V_{mm}'s obtained for alkanes and their mixtures[4] shows, that the respective values are fairly close to each other. Small differences may be explained by approximations in the numerical procedures and also by the simple fact, that the data for alkanes refer to a temperature 5K lower.

A stringent test of any approach to the liquid state is its ability to predict excess functions of mixing. Using the parameters from Table 2, i.e., exactly the

TABLE 3

Excess volumes for equimolar mixtures at 298.15K

		V^E, cm^3 mol^{-1}			
r_i	r_i	Experimental	$\ell = 0$	$\ell = 1$	$\ell = 2$
1	2	0.008	0.026	–	–
1	3	0.050	0.066	–	–
1	4	0.074	0.101	–	–
1	6	0.116	0.156	–	–
1	8	0.156	0.195	–	–
1	10	0.178	0.223	–	–
2	3	0.008	0.009	0.014	–
2	4	0.012	0.026	0.035	–
2	6	0.036	0.060	0.070	–
2	8	0.060	0.088	0.095	–
2	10	0.088	0.109	0.112	–
3	4	-0.002	0.004	0.005	0.011
3	6	0.019	0.023	0.023	0.043
3	8	0.051	0.042	0.040	0.066
3	10	0.089	0.059	0.053	0.082
4	6	0.011	0.007	0.007	0.011
4	8	0.041	0.020	0.018	0.025
4	10	0.078	0.032	0.027	0.037
6	8	0.010	0.003	0.003	0.003
6	10	0.037	0.009	0.007	0.009
8	10	0.007	0.002	0.001	0.001

[a] Ref. 3

same values that served to describe the volumes of pure components, we have calculated the excess volumes of mixing V^E of binary equimolar mixtures. The results are listed in Table 3. The experimental data are those given by Benson and Pflug.[3] The agreement is reasonable even for mixtures containing methanol. A strict comparison of deviations would not be meaningful, in review of an approximate character of the computational procedures; moreover, different sets of mixtures are described by formulas for different ℓ. For larger V^E values, however, such as for propanol + decanol, slight improvement is observed along with increasing ℓ. In general, for molar volumes we seem to be able to achieve the stated objectives: the association of alcohols notwithstanding, it is possible to predict the properties of mixtures in terms of the quantities characterizing pure components. Three parameters, obstainable essentially from values for 3 substances, if measured accurately, serve to describe both the volumes of pure liquids and of 21 liquid mixtures.

Isobaric expansivities

The results of the calculations performed also for 298.15K using Eqs. (8-10) are

TABLE 4

Isobaric expansivities at 298.15K

	$10^3\ \alpha$, K^{-1}	
r	Experimental	$\ell = 0$
1	1.202[b] 1.185[a]	1.217
2	1.088[b] 1.083[a]	1.068
3	0.994[b] 0.981[a]	0.984
4	0.937[a]	0.929
5	–	0.891
6	0.852[a]	0.863
7	–	0.841
8	0.818[a]	0.824
9	–	0.810
10	0.804[a]	0.798

[a] Ref. 3

[b] Obtained from density expansions $\rho(T)$ given in International Critical Tables, Vol. 3.

given in Table 4. The calculations were made for $\ell = 0$ only, in view of limited accuracy of the experimental data (sufficiently precise values are missing even for some pure components, and no excess functions of mixing α^E were found). For consistency, values of αV were obtained using the computed V data for $\ell = 0$ as listed in Table 1. The respective parameters are $(\alpha V)_1 = 0.02234$ cm^3 K^{-1} mol^{-1}, $(\alpha V)_2 = 0.10190$ cm^3 K^{-1} mol^{-1}, and $(\alpha V)_3 = 0.07505$ cm^3 K^{-1} mol^{-1}; the first of this values may be compared with $(\alpha V)_{mm}$ in (4). Using these three parameters together with these in Table 2, prediction of α^E is, of course, possible.

Isothermal compressibilities

Analogous calculations were performed. The respective parameters are $(\kappa_T V)_1 = 0.01689$ J^{-1} cm^6 mol^{-1}, $(\kappa_T V)_2 = 0.10684$ J^{-1} cm^6 mol^{-1}, and $(\kappa_T V)_3 = 0.08313$ J^{-1} cm^6 mol^{-1}. The value of $(\kappa_T V)_1$ for methylene interactions may be compared with $(\kappa_T V)_{mm} = 0.01751$ J^{-1} cm^6 mol^{-1} for n-alkanes at 293.15K,[4] demonstrating again physical meaningfulness of our parameters. The results are shown in Table 5. The parameters in the Table labelled "experimental", have been calculated by Benson and Pflug[3] using specific heats and sound velocities. In view of the accuracy of these data, the agreement with the values calculated through our procedure is entirely satisfactory.

Adiabatic compressibilities

These have been calculated by Benson[8] from sound velocity data. The respective values computed in the same way as for the quantities considered above, are given in Table 6. The parameters are $(\kappa_S V)_1 = 0.01499$ J^{-1}cm^{6}mol^{-1},

TABLE 5

Isothermal compressibilities at 298.15K

r	$10^3\ \kappa_T$, J^{-1}cm^3 Experimental[a]	$\ell = 0$
1	1.247	1.276
2	1.150	1.127
3	1.012	1.018
4	0.933	0.939
5	–	0.881
6	0.832	0.837
7	–	0.802
8	0.779	0.773
9	–	0.750
10	0.729	0.730

[a] Ref. 3

$(\kappa_S V)_2 = 0.08844\ J^{-1} cm^6 mol^{-1}$, and $(\kappa_S V)_3 = 0.07138\ J^{-1} cm^6 mol^{-1}$. Obviously, the conclusions reached above are also applicable to the case of adiabatic compressibilities.

TABLE 6

Adiabatic compressibilities at 298.15K

r	$10^3\ \kappa_S$, $J^{-1}\ cm^3$	
	Experimental[a]	$\ell = 0$
1	1.038	1.056
2	0.966	0.950
3	0.862	0.866
4	0.796	0.804
5	–	0.785
6	0.720	0.722
7	–	0.693
8	0.677	0.670
9	–	0.651
10	0.632	0.635

[a] Ref. 8

Heats of mixing

As Eq. (1) applies to both U^C and V, at constant pressure it applies also to the sum $H^C = U^C + PV$. Making the usual assumption that the heat of mixing is determined by interactional contributions only, for a mixture of substances i + j one simply has $H^E = H^C - x_i H^C_{ii} - x_j H^C_{jj}$, where the quantities without subscripts refer to mixture and double subscripts to pure components. The problem, thus, is that of finding H^C, H^C_{ii} and H^C_{jj}, or U^C, U^C_{ii} and U^C_{jj}. To do this we can represent the configurational energy by

$$U^C = \frac{-E}{V^n} \tag{11}$$

where E is a constant, and the equation is clearly applicable also to pure substances. Then, by thermodynamics,

$$U^C = -\frac{V}{V^n}\,(T\,\gamma - P) \tag{12}$$

where $\gamma = \alpha/\kappa_T$. Also

$$n = \frac{V(T\gamma - P) - P\left(\dfrac{BP}{Nk} + T\right)\dfrac{dB}{dT}}{H^{vap} - P\left(\dfrac{NkT}{P} + B - V\right)} \tag{13}$$

where H^{vap} is the enthalpy of vaporization. The consequences of Eqs. (11) and (13), with the second virial coefficient of the vapour B being neglected, have been considered by a number of authors, most recently by Bagley and his collaborators.[9] Equations (12) and (13) together suggest a way for the experimental determination of U^C. In view of the fact, however, that for either components or mixtures, U^C is several orders of magnitude larger than U^E or H^E, very accurate values of all parameters featured in Eq. (13) are necessary for the prediction of heats of mixing.

The values of γ were available immediately from the data given above. The heats of vaporization of the lower alcohols have been measured by several authors, most recently and accurately by Polak and Benson.[10] For the second virial coefficients we have utilized an observation of Foz *et al*[11] that for the lower alcohols, plots of B/V_c vs. T/T_c, where the subscript c refers to the liquid-vapour critical point, gives nearly a single curve, or a family of curves close to one another. We have therefore determined from experimental data the coefficients in the expression $-B/V_c = d_0 + d_1 \, T/T_c + d_2(T/T_c)^2$; for ethanol, we have taken the B data recomended by Dymond and Smith,[12] while for propanol we have used the data of Foz *et al.*[11] and Cox;[13] the critical constants compiled by Zwolinski and his colleagues[14] were used. For ethanol, the constants $d_0 = 361.5$, $d_1 = -931.3$ and $d_2 = 604.9$ give $B(298.15\ K) = -4251\ cm^3mol^{-1}$. For propanol, the respective constants are 70.9, −165.4 and 100.0, which lead to $B(298.15\ K) = -2170\ cm^3mol^{-1}$; using Cox's own equation, logarithmic in form, one obtains $-2177\ cm^3mol^{-1}$; such an agreement increases confidence in our B/V_c formula used for ethanol.

The parameters so obtained were substituted into Eqs. (12) and (13). The resulting values are $H^C = -42903 J\ mol^{-1}$ for ethanol and $-43974\ J\ mol^{-1}$ for propanol. Similar calculations for higher alcohols could not be performed for lack of the appropriate experimental data, in particular of the second virial coefficients at room temperature. We have therefore combined the values for ethanol and propanol with the excess heats of mixing and generated on a computer sets of H^C values for pure components for $\ell = 0$. The parameters which reproduce the H^c values given above for ethanol and propanol are $H_1^C = -2599\ J\ mol^{-1}$, $H_2^C = -84120\ J\ mol^{-1}$, and $H_3^C = -43289\ J\ mol^{-1}$. The calculated values of H^E for equimolar binary mixtures, obtained using this set of parameters, are given in Table 7, along with the experimental data of Benson and Pflug.[3] In view of difficulties involved in calculating H^C values for pure components, there was little point in performing calculations for $\ell > 0$. Inspection of Table 7 shows that with 3 interaction parameters it is possible to describe 21 binary systems. Numerical differences between calculated and experimental values may be explained in terms of differences in force fields around, say, a methanol molecule (cf. the discussion above in section 3) and, say, a decanol molecule.

TABLE 7

Equimolar excess heats of mixing at 298.15K

		H^E, J mol^{-1}		
r_i	r_j	Experimental[a]	C Corr. volumes	$\ell = 0$
1	2	4.5	23.5	45.7
1	3	82.1	139.3	114.1
1	4	142.4	204.4	176.4
1	6	236.1	321.3	271.8
1	8	337.6	432.9	339.0
1	10	397.4	493.9	387.9
2	3	19.2	23.3	16.3
2	4	48.1	33.5	45.7
2	6	126.4	100.6	104.3
2	8	217.5	165.9	152.2
2	10	301.0	245.1	189.7
3	4	5.4	5.3	7.6
3	6	61.5	51.8	40.0
3	8	153.5	142.1	73.2
3	10	252.1	246.5	101.7
4	6	27.0	31.9	13.0
4	8	103.8	114.4	34.8
4	10	201.3	215.5	56.0
6	8	26.0	27.1	5.4
6	10	95.6	103.9	15.8
8	10	22.4	20.8	2.8

[a] Ref. 3

Table 7 contains also values labelled "corresponding volumes" obtained from the relation $H^E = aV^E$, where a is a constant. This is the simplest possible expression, based on the principle of corresponding volumes proposed before.[4] The value of $a = 2770$ J cm^{-3} was simply obtained as an arithmetic average for pairs with $r_j > r_i \geqslant 3$. The usefulness of this principle for the present case may be judged easily from the Table. Clearly, using more terms in the $H = H(V)$ expansion should improve further the agreement.

5. SOME CONCLUDING REMARKS

Apart from monatomic molecules and their mixtures, systems of alkanes are usually considered to be the simplest. Normal alkanes and their binary mixtures have been treated in the paper quoted before;[4] the degree of difficulty was quite evidently less than that for mixtures of alcohols. It was possible to predict functions like excess compressibility within the limits of experimental accuracy.

The improvement caused by increasing ℓ for n-alkanes was unmistakeable.

In increasing degree of complexity, mixtures of alkanes with aromatic hydrocarbons are usually taken as the next class of systems. In this instance, difficulties are encountered, even if a description of a series of systems with a single set of quasi-lattice theory parameters was possible.[15]

In the context of the studies just mentioned, the relative success of the present treatment is clearly, to a certain extent, due to the fact that no "foreign" molecules "disturbing" the alcohol medium are present in our systems. However, the application of the present approach to mixtures containing alcohols together with other substances now appears feasible. While the number of characteristic parameters is in general due to increase, such an increase might be insignificant, just as it was possible in this investigation to reduce the number of F_{yy1}, parameters from six to three.

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References

1. Nakanishi, K. and Shirai, H., *Bull. Chem. Soc. Japan* 43, 1634 (1970).
2. Diaz Peña, M. and Fernandez Martin, F., *An. Real Soc. Esp. Fis. Quim.* B59, 323, 331 (1963); ibid., B60, 9 (1964).
3. Pope, A. E., Pflug, H. D., Dacre, B. and Benson, G. C., *Can. J. Chem.* 45, 2665 (1967); Pflug, H. D., Pope, A. E. and Benson, G. C., *Can. J. Chem.* 46, 287 (1968); Benson, G. C. and Pflug, H. D., *J. Chem. Eng. Data*, 15, 382 (1970).
4. Brostow, W., *Phys. Chem. Liquids* 3, 91 (1972).
5. Harary, G., *Graph Theory*, Addison-Wesley, Reading, Mass., (1969).
6. Brostow, W. and Schinzel, A., *J. Statist. Phys.* 4, 103 (1972).
7. Hill, T. L., *Statistical Mechanics*, McGraw-Hill, New York, (1956), Chapter 6.
8. Benson, G. C., private communication.
9. Bagley, E. B., Nelson, T. P., Barlow, J. W. and Chen, S. A., *Ind. Eng. Chem. Fundam.* 9, 93 (1970).
10. Polak, J. and Benson, G. C., *J. Chem. Thermod.* 3, 235 (1971).
11. Foz, O. R., Morcillo, J., Masia, A. P. and Mendez, A., *An. Real Soc. Esp. Fis. Quim.* 50B 23 (1954).
12. Hanks, P. A. and Lambert, J. D., unpublished, quoted by J. H. Dymond and E. B. Smith, *The Virial Coefficients of Gases*, Clarendon Press, Oxford, 1969.
13. Cox, J. D., *Trans. Faraday Soc.* 57, 1674 (1961).
14. Kudchadker, A. P., Alanis, G. H. and Zwolinski, B. J., *Chem. Revs.* 68, 659 (1968).
15. DeQ. Jones, H. K., Poon, D. P. L., Lama, R. F. and Lu, B. C. Y., *Can. J. Chem. Eng.* 45, 22 (1967).