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VAPOUR–LIQUID EQUILIBRIA IN ALKAN-1-OL +
n-ALKANE MIXTURES

(Technical Report)

Prepared for publication by

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Vapour–liquid equilibria in alkan-1-ol + \textit{n}-alkane mixtures (Technical Report)

Abstract - Recommended values are given for vapour-liquid equilibria, excess molar enthalpies, excess molar heat capacities, liquid-liquid equilibria, excess molar volumes, activity coefficients at infinite dilution and solid-liquid equilibria for binary alkan-1-ol + \textit{n}-alkane mixtures. In addition, recommended values are reported for certain properties of the pure components: volumetric properties of gases, orthobaric liquid densities, compressibilities, critical properties, heat capacities, vapour pressures and enthalpies of vaporization.

INTRODUCTION

The purpose of this Project was to coordinate international efforts for the measurement, correlation and understanding of thermodynamic data for alkan-1-ol + \textit{n}-alkane binary mixtures. These systems were selected because of their technological importance as well as for their scientific interest. The aim was to develop a consistent set of recommended values for low-pressure vapour-liquid equilibrium and related properties. These recommended values were to be based as far as possible on reliable experimental measurements. The following important pure component and mixture properties were identified and working groups were set up to concentrate on each of these:

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The various stages in this project for each individual property were:

1) collection of a complete bibliography
2) collection of numerical data.

The emphasis was on experimental measurements but where there was a reliable predictive method for members of an homologous series, then this was used to give values for members where no experimental measurements were available.

3) assessment of experimental data.

Data that have been critically evaluated were generally either rejected or selected. There were some data for which a critical assessment was not possible because of a lack of information. Such data were retained until additional information became available.

4) recommended values.

A preliminary evaluation was carried out using the selected, and retained, data, by different members of each working group. Different sets of recommendations were then compared and agreed values produced with uncertainty limits. Values for different properties were tested for consistency and adjustments made to individual values and to the estimated uncertainties until there was agreement.
Vapour-liquid equilibria in alkan-1-ol + n-alkane mixtures

Mixtures were restricted to C₁ to C₁₀ alkanols and C₅ to C₁₆ n-alkanes. This gives 120 binary mixtures for which it was recommended that a full set of references and numerical data should be collected. In this way it was possible to identify important mixtures for which experimental measurements were required. For detailed consideration, attention was restricted to five key systems, selected for the relative differences in carbon chain length of the components, and differences in the strength of hydrogen bonding in the alkanol. These were:

- methanol + hexane
- ethanol + hexane
- ethanol + hexadecane
- butanol + decane
- hexanol + hexane

Over sixty scientists worldwide participated in this project and a series of regular Workshops was organized for participants to meet and to discuss progress. The programmes for these meetings included:

- communications on original work (results of experimental measurements and theoretical investigations)
- data correlations
- state of the art reviews
- working party reports
- computer packages, data bank and data base demonstrations
- discussions on data exchange
- recommendations of values for individual properties
- results of consistency tests.

The First Workshop was held just outside Warsaw in 1984, with subsequent Workshops in Paris (1985), Budapest (1987), Thessaloniki (1988), Gradisca d'Isonzo (1989) and Liblice (1991). In view of the industrial importance of these and related mixtures the Thessaloniki Workshop had a special session on Applications, with talks and discussions on environmental and commercial aspects.

Many of the papers presented at these meetings were published as special issues of journals (Fluid Phase Equilibria 27, 1-202 (1986); 42 1-305 (1988); 56 1-361 (1990) and 89 1-252 (1993) and Pure and Applied Chemistry 61, 1362-1460 (1989)). In addition a number of papers were published independently.

The results of the critical evaluations and recommended values for individual pure component and mixture properties are as follows.

**PURE COMPONENT PROPERTIES**

**Volumetric properties of gases**

Dymond et al. (ref. 1) recommended second virial coefficient values for the n-alkanes up to n-octane, following a critical review of all available experimental data. A polynomial equation in powers of 1/T was used to represent the values. In a later paper, Tsonopoulos et al (ref. 2) revised the recommendations for n-butane, n-pentane and n-hexane using more recent experimental data. The recommended virial coefficients can be satisfactorily correlated using either the Hayden-O’Connell correlation (ref. 3) or the Tsonopoulos correlation (ref. 4) at temperatures below 0.65 times the critical temperature, but the Tsonopoulos correlation is better at higher reduced temperatures. For estimation of second virial coefficients for n-alkanes above C₈ using these correlations, it is essential to use values for the critical temperature and critical pressure which were recommended by Ambrose and Walton (ref. 5) rather than values given in the DECHEMA publication (ref. 6).
Recommended second virial coefficients were given by Tsonopoulos et al. (ref.2) for alkan-1-ols from methanol to butan-1-ol. The values are well correlated with parameter $a = 0.0878$, as in the original Tsonopoulos paper (ref.4) but for methanol parameter $b = 0.064$ gave a better fit than the original figure of 0.056. The reanalysis supports the earlier observation that $b$ has a weak dependence on reduced dipole moment, but accurate virial coefficient measurements on $C_4^+$ alkan-1-ols are required to confirm this and provide a sound basis for calculation of second virial coefficients for higher members of this series.

For binary mixtures of alkan-1-ols plus $n$-alkanes, analysis of the experimental data showed that the Tsonopoulos correlation gave a good fit with the prescribed mixing rules (ref. 4). The only additional parameter, $k_{ij}$, which is introduced to account for departure of the mixture critical temperature from the geometric mean value, was shown to have an average value of 0.16±0.03 (ref. 7), but it is recommended that values for specific mixtures should be taken from Fig. 7 of ref. 2 for calculation of second virial cross-coefficients.

**Orthobaric liquid densities, compressibilities**

A critical analysis (ref. 8) of saturated liquid density data for $n$-alkanes and alkan-1-ols in the literature resulted in the rejection of 157 points (out of 1584) for $n$-alkane density and 747 (out of 2617) for alkan-1-ols. The retained values were represented in terms of the critical density $p_c$ by the equation

$$\frac{\rho}{p_c} = 1 + \sum_{i=1}^{N} a_i (1-T/T_c)^{(i/3)}.$$  

Tables of values of the coefficients $a_i$ were given, together with the temperature range of applicability (typically from the normal melting-point, or a few degrees above it, to within a few degrees of the critical temperature), and the absolute and relative root mean square deviations.

The temperature dependence of the derived thermal expansion coefficient along the saturation curve was examined to determine whether there were any obvious inconsistencies in the recommended density values. Some deviation from the expected behaviour was reported for certain compounds over sections of the temperature range.

**Critical properties**

Measurements of critical temperatures and critical pressures have been carefully assessed (ref. 9). For higher members of each series, above $n$-decane and pentan-1-ol, decomposition can seriously affect the results. Smooth plots were given for these properties against carbon number with the exception of the first member of each series (the critical pressure of methane and the critical temperature of methanol). The observed critical pressure of $n$-tetradecane was clearly in error. Recommended values are given for the critical temperatures and pressures and the results represented by different equations.

For the critical temperatures of $n$-alkanes, Riedel (ref. 10) found that the quantity $X = T_b/(T_c-T_b)$, where $T_b$ is the normal boiling-point, varies linearly with carbon number. Ambrose (ref. 11) found that, with $n$ the carbon number,

$$X = 1.242 + 0.138n.$$  

Although this is a purely empirical correlation, it gives the best fit to the recommended values.
A different form of equation, originally proposed by Kreglewski (ref. 12), also fits the recommended values, though there are slightly larger differences with the lower n-alkanes:

\[ \ln(960-T_c/K) = 6.8162 - 0.2115 \frac{n^2}{3}. \]

These two equations diverge at carbon numbers above 20.

For the critical pressures, Ambrose (ref. 13) revised the equation used by Lydersen (ref. 14). It was found that

\[ \frac{(M/k\text{g mol}^{-1})^{1/2}}{(P_c/\text{MPa})^{1/2}} = 0.0339 + 0.0226n \]

where \( M \) is the molar mass.

There are far fewer critical property values for alkan-1-ols, and so recommended values were obtained for higher members by relating the critical temperatures and pressures of all alkan-1-ols to those of the n-alkanes, with the assumption that as the chain length increases so the effect of the -OH group would become progressively less. The critical temperature for higher alkan-1-ols was given in terms of the value for the corresponding n-alkane \( T_{\text{alk}} \) by the following equation:

\[ \frac{T_c}{T_{\text{alk}}} = 1 + 1.576/n^{1.14}. \]

It was pointed out that the calculated values are not very sensitive to changes in \( n \).

An alternative expression for the relationship between the critical temperatures of n-alkanes and alkan-1-ols was presented by Rosenthal and Teja (ref. 15):

\[ T_c/K = T_{\text{alk}}/K + 833.0959/(2.015476 + n). \]

There is close agreement between these two representations. Even for hexadecan-1-ol the difference in critical temperature would be only 2 K.

The critical pressure of the alkan-1-ols was related to that of the n-alkane with the same carbon number by the equation

\[ \frac{P_c}{P_{\text{alk}}} = 1 + 0.284/n^{0.3} \]

**Heat capacities of liquids**

The results of a critical evaluation of the heat capacities of liquid n-alkanes have been reported by Ruzicka Jr. et al. (ref. 16), and for alkan-1-ols by Zabransky et al. (ref. 17). Tables for each compound give, for each reference, the temperature range of the measurements, a note of whether the measurements were for saturation or isobaric heat capacity, the calorimeter type, purity of compound and method of purity determination, and possible error in the data as estimated by the authors. A separate Table indicates which data sets were selected for the correlation. A third Table for each compound gives the coefficients in the cubic spline polynomials used to represent the temperature dependence of isobaric and saturation heat capacities over specified sub-intervals of temperature. Overall statistics are given for the fits. Neighbouring polynomials have at their common limit identical values for the heat capacity and the same first and second derivatives. Estimates of accuracy are given to the values generated by these cubic splines, and recommended values generated from the parameters of these equations are tabulated at 273.15 K, 298.15 K, and at 10 K intervals over the whole of the temperature range of the selected experimental data. Comparisons with the selected data are shown in individual deviation plots for each compound.
Vapour pressures
The recommended equation for the representation of the liquid vapour-pressure curve is the four-constant form proposed by Wagner (ref. 18):

\[ \ln(P/P_c) = (at + bt^{1.5} + ct^{2.5} + dt^5)/T_r \]

where \( t = 1 - T_r \), and \( T_r = T/T_c \).

This series is found to be always highly convergent (ref. 9) when the equation is fitted to a long-range set of good data, and the remaining terms are correction terms that introduce curvature to the straight line resulting from the first term. Each term has a smaller effect than its predecessor, except for certain compounds at very low reduced temperature.

Vapour pressure data for \( n \)-alkanes are of good quality over wide temperature ranges for compounds up to \( n \)-octane, and the coefficients derived from the data fit give a smooth variation with carbon number (ref. 9). For higher \( n \)-alkanes, there are measurements around atmospheric pressure together with critical properties. The fits obtained were adjusted slightly in certain instances to obtain a consistent variation in the values for the coefficients with carbon number for these compounds also. Values are tabulated for the coefficients. Plots of the deviation from the first linear term are shown to give a regular family of curves.

For the alkan-1-ols, there is not the same regularity in the vapour-pressure curves, or in the tabulated coefficients of the fitting equation, as for the \( n \)-alkanes. However, if the equations are differentiated to give enthalpy of vaporization divided by compression factor then regularity is apparent with a smooth variation in the position of the minimum on ascending the series, apart from methanol.

As a result of multi-property fitting, using liquid heat capacity and vapour pressure data, Craven and de Reuck (ref. 19) concluded that an 'inverted' form of equation for the vapour pressure was preferable in the case of methanol:

\[ \ln(P/P_c) = T_r(a\theta + b\theta^{1.5} + c\theta^2 + d\theta^{2.5}) \]

where \( \theta = T_c/T - 1 \). Values were given for the coefficients \( a, b, c \) and \( d \).

Enthalpies of vaporization
Recommended values for enthalpies of vaporization for \( n \)-alkanes and alkan-1-ols have been given by Majer and Svoboda (ref. 20) in their critical review of enthalpy of vaporization data for organic compounds.

MIXTURE PROPERTIES

Vapour-liquid equilibria
A critical evaluation of vapour-liquid equilibrium data has been made (ref. 21) for 320 data sets for 53 binary alkan-1-ol + \( n \)-alkane mixtures, using a multistep testing procedure. A grid with the distribution of data sets shows that measurements are confined mainly to mixtures of \( C_5 \) to \( C_{11} \) \( n \)-alkanes with alkanols from methanol to pentanol and octan-1-ol, plus mixtures of \( n \)-hexane + hexan-1-ol and decan-1-ol with \( n \)-hexane.

The VLE data were all tested for thermodynamic consistency using the extended pressure dependent area test and the infinite dilution test, followed by data reduction and comparison with enthalpy of mixing data.

For each data set there is reported the reference, the \( P, T, y \) conditions (isothermal/isobaric/vapour phase composition), the overall diagnostic (consistent,
inconsistent or uncertain), the experimental pressure/temperature and number of points, the results of individual thermodynamic consistency tests and the results for the most effective correlation equation giving the number of coefficients, number of sign changes for residuals in $y$ and relative standard errors in pressure or temperature.

The Table includes results for the five key systems. As an Appendix, values for activity coefficients and excess Gibbs energy are given which have been recalculated using the rational equation parameters fitted to the original recommended data sets. Estimates of the corresponding standard deviations are also given.

**Liquid-liquid equilibria**

The results of a critical evaluation of solubility data for binary systems of methanol with $n$-alkanes have been reported by Skrzecz (ref. 22). Values for solubility, mutual solubility and upper critical solution temperature which often differ significantly from author to author were carefully assessed. As a result, certain data sets were selected. Mutual solubilities were represented by the equation:

$$T = a_0 + \sum_{i=1}^k (a_i b_i)^2$$

where $b_i = (x_1/x_1^c - x_2/x_2^c) / (x_1/x_1^c + x_2/x_2^c)$.

$T$ is absolute temperature, $k<4$ in most cases, $a_0$ is the upper critical solution temperature, $x_i$ is mole fraction of component $i$ and superscript $c$ gives the compositions at UCST.

A more precise representation of the data was given by consideration of the hydrocarbon-rich and methanol-rich phases separately, and coefficients are tabulated accordingly. The UCST, $a_0$, and the critical composition were found to vary smoothly with carbon number of the $n$-alkane, and were expressed by:

$$a_0 = 140.47 + 60.45 \ln n + 11.564 n - 0.3116 n^2$$

$$x_1^c = -0.132 + 0.405 \ln n - 0.0072 n$$

**Excess molar volumes**

A review of the excess molar volume data, given by Treszczanowicz et al (ref. 23), covers 54 systems and 207 data sets published up to 1991. A grid with carbon numbers of $n$-alkane and alkan-1-ol is used to indicate the data sets that were selected. For each of these data sets, the temperature, pressure and composition range of the measurements are tabulated, together with a note of the number of points, the smoothing equation that gives the best data fit and values for the coefficients, the equimolar value for the excess molar volume, the standard and maximum deviation of the fit and the experimental technique and reference. There is a noticeable lack of data for mixtures of alkan-1-ols with $n$-pentane, and with $n$-alkanes longer than $n$-decane, and for mixtures of $n$-alkanes with heptan-1-ol and nonan-1-ol.

Excess volumes for alkan-1-ol $+ n$-alkane mixtures are characterized usually by high asymmetry and positive and negative shape. For the selected data sets, the best fitting equation (usually that of Neau, Myers-Scott or Redlich-Kister) needs a maximum of six parameters. However, in the highly dilute alkanol region, the data are best treated by a polynomial. This allows a more accurate extrapolation to infinite dilution for estimation of the limiting value $V_t^{E,\infty}$. 
There are six systems where the recommended $V^E$ values have the highest accuracy and these include two key mixtures ethanol + n-hexane and hexan-1-ol + n-hexane. A further twelve systems have high quality experimental data, which require confirmation by measurements from other sources. Data on the three other key mixtures in the project are of lower accuracy.

**Excess molar heat capacities and enthalpies**

Attention has been focussed (ref. 24) on the five mixtures methanol + n-heptane, ethanol + n-heptane, ethanol + n-hexadecane, butan-1-ol + n-decane and hexan-1-ol + n-hexane, with new $C_P^E$ measurements reported for the last three mixtures and literature data on excess molar heat capacities and excess molar enthalpies critically assessed, and combined with these measurements to produce recommended sets of values for these mixtures. The same equation was used to represent the recommended values for each property:

$$y^E = x(1-x)[\sum l=0\ A_l(1-2x)^l + (1-e^{-Z/x}) \sum j=0 \ B_j x^j]$$

The advantage of this form of equation is that it will fit the data over the whole composition range, even in the very dilute region where the usual Redlich-Kister type of equation fails. For these mixtures, $i$ has a maximum value of 3 but generally only two or three of the terms are required; $j$ has a maximum value of 1. Values are given for the coefficients. Standard deviations for the fits are in accord with the corresponding experimental uncertainties - excess enthalpies are known to within ±5 J mol⁻¹ and excess heat capacities are given to better than ± 0.2 J K⁻¹ mol⁻¹.

**Activity coefficients at infinite dilution**

A survey of critically evaluated experimental limiting activity coefficients in alkan-1-ol + n-alkane mixtures has been given by Dohnal et al (ref. 25). Up to that time, only 57 of the possible solute-solvent pairs had been studied (24%), with measurements focussed mainly on short chain alkan-1-ols with short chain n-alkanes or n-hexadecane. Half of all the data are for just ten solute-solvent pairs. Most measurements are close to ambient temperature. As a result of different volatility conditions in the different mixtures, a variety of experimental methods has been employed. The critical evaluation had to take into account the accuracies of the technique which was used. Accuracy grades were assigned to individual data sets which give consistency between the different sets for a given system. Comparisons were made of the temperature dependence of the limiting activity coefficients with calorimetric excess enthalpy data, where available, and trends in values for homologous series were also used to discriminate between conflicting values. The conclusion is that by far the majority of the values have uncertainties as large as 10-20% and that further, more accurate, measurements are required.

**Solid-liquid equilibria**

A systematic investigation of solid-liquid equilibria in alkan-1-ol + n-alkane mixtures was carried out by Plesnar et al. (ref.26-29) and results reported for octan-1-ol + n-octane or n-decane or n-undecane or n-dodecanes or n-hexadecane and butan-1-ol + n-octane or n-decane. The accuracy of the solubility temperatures from the cooling and warming curves is estimated to be ±0.05 K, but on the steep parts of the curve ±0.5 K. The results were very satisfactorily correlated with the NRTL and NRTL-MK equations, with the latter giving a slightly better fit.
Table 1. Availability of experimental data for alkan-1-ol + n-alkane mixtures. n and m give the number of carbon atoms in the chain for alkanes, alkanols respectively.

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For the pure components, thermodynamic consistency would be assured if all the recommended values for the various properties were used to construct an equation of state, from which other properties could be obtained by mathematical manipulation. This is a lengthy task and, of the compounds in this project, it has been carried out only for methanol. Craven et al (ref. 30) developed a reduced Gibbs energy function for the gas phase and, more recently, de Reuck and Craven (ref. 31) have constructed a reduced Helmholtz energy function for the representation of properties over all gaseous and liquid states.

One important aspect of this Project is that it has identified those areas - systems and properties - where experimental data are lacking. This can be clearly illustrated by means of the grid shown in Table 1 which indicates the mixtures for which data are available for the excess molar volume (V), excess molar enthalpy (H), excess molar heat capacities (C_P) and vapour-liquid equilibria (VL).

Table 2. Availability of experimental liquid-liquid equilibria data (LLE) for alkan-1-ol + n-alkane mixtures. n and m give the number of carbon atoms in the chain for alkanes, alkanols respectively.

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The availability of data for liquid-liquid equilibria (LLE) is shown in Table 2. The systems for which there are data for activity coefficients at infinite dilution are given in Table 3.
Table 3. Availability of experimental activity coefficient data at infinite dilution for alkan-1-ol + n-alkane mixtures. m indicates C_m alkanol in n-alkane and n represents C_n n-alkane in alkan-1-ol.

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where 1 indicates a single datum, and s refers to several data points.

The final recommendations, based upon experimental measurements, provide a critical test for various empirical equations and theoretical approaches developed on the basis of a molecular model. This project stimulated much theoretical work by different research groups dealing with the same particular problem, and this was an additional successful outcome of this series of IUPAC workshops on alkan-1-ol + n-alkane mixtures. It has led to a deeper understanding of the thermodynamics of these mixtures on a molecular basis.

Nagata and Miyamoto (ref. 32) correlated vapour-liquid equilibrium data and excess enthalpy data for selected alkan-1-ol + n-alkane mixtures using the UNIQUAC associated-solution model. Values are given for the association constants and enthalpies of hydrogen bond formation from different methods.

Arai et al (ref. 33) showed that a good correlation of the recommended liquid-liquid equilibrium data was given by the Wilson equation when the binary interaction parameters were represented as a function of temperature. For multi-property correlation, Heintz (ref. 34) introduced the ERAS model (extended real associated solution model) for alkan-1-ol + n-alkane mixtures. This combines a real associated solution model with Flory's equation of state. It assumes that only consecutive linear association of the alkan-1-ols occurs, and that this can be represented by a chemical equilibrium constant which is independent of the chain-length of the associated species. Calculations of $H^E$, $V^E$, and $G^E$(VLE) for the five key systems at 298.15 K and 323.15 K (ref. 35) gave an almost quantitative description of the experimental data, with the exception of activity coefficients at infinite dilution, using only three adjustable physically significant parameters. However, it was found that different values for the entropy parameter have to be used to describe VLE and LLE for methanol + n-hexane and ethanol + n-hexadecane properly. Liu et al (ref. 36,37) presented a different model, containing chemical and physical terms. Chain
association in the alkan-1-ols was assumed to be relatively weak for dimers, to increase for the formation of trimers and tetramers, and to decline slowly as the chain length further increased. Cyclic association to form tetramers was also included. The physical terms account for size differences and differences in interaction energies, with configuration and group surface interaction contributions in the expressions for the activity coefficient. Values for the group interaction parameters and their temperature and pressure derivatives were obtained by an elaborate iterative procedure. The resultant data fits for $H^E$, $C_pE$, $V^E$ and $G^E$ are very satisfactory.

The LFAS (Lattice Fluid Associated Solutions) model was shown by Panayiotou (ref. 38,39) to be rather satisfactory for the description of thermodynamic data for pure alkan-1-ols and not-too-dilute alkan-1-ol + n-alkane mixtures. This model is not predictive in that the three pure-component parameters, the three association parameters and the three binary parameters have to be determined from experimental data. However, once values for the binary parameters are known for one temperature, they can be used at other temperatures. The model has been extended using group-contribution formalism (ref. 40). Experimental data are required to estimate the model parameters but now they may be used to describe an entirely different system. All alkan-1-ols and n-alkanes may be formed out of CH$_3$, CH$_2$ and OH groups, and Lattice Fluid characteristic parameters are given for these groups, together with binary group interaction parameters, derived from experimental data on selected pure components and binary mixtures. The degree to which the model can represent/predict the pure component properties is indicated by the average absolute percent deviations which for nine n-alkanes and three alkan-1-ols are: 2.6% for vapour pressure, 3.1% for enthalpy of vaporization and 1.6% for liquid density. For nine alkan-1-ol + n-alkane mixtures, the average absolute percent deviations are 13.2% for $H^E$, 25.2% for $V^E$ and 1.8% for isothermal vapour-liquid equilibrium pressures.

In order to correlate caloric data with PVT data, Dieters (ref. 41) used his equation of state (ref. 42,43) with a chain association theory for the simultaneous calculation of $H^E$, $V^E$ and VLE for four of the five key systems. Pure component parameters were derived from values of critical properties, vapour pressures and liquid densities. Values are given for these and for the binary interaction parameters determined from the mixture data. The excess enthalpy, excess molar volume and VLE calculations agree with experimental data reasonably well, although there is an exaggerated tendency towards liquid-liquid phase splitting. This approach has great potential over wider temperature and pressure ranges.

Acknowledgements

It is a pleasure to acknowledge the enthusiasm of all who participated in the organization of this project, the members of the IUPAC Subcommittee on Thermodynamic Data and especially Henry Kehiaian, who saw the project off the ground and through its first few years; the friendly cooperation of Professor Bylicki and Dr. A. Maczynski of CODATA whose Symposia on Critical Evaluation and Prediction of Phase Equilibria in Multicomponent Systems were held jointly with our workshops; the excellent organization of all the local organizing committees under Dr. A. Maczynski (Warsaw, 1984), Dr. H.V. Kehiaian (Paris, 1985), Dr. S. Kemeny (Budapest, 1987), Dr. C.G. Panayiotou (Thessaloniki, 1988), Prof. P. Alessi (Gradisca d'Isonzo, 1989) and Prof. R. Holub (Liblice, 1991); and finally the support and continued interest of the sixty or so scientists who were involved in this project.

REFERENCES


