Thermochimica Acta, 62 (1983) 113–124
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

THE PREDICTION OF VAPOR–LIQUID EQUILIBRIUM FROM HEAT OF MIXING DATA OF BINARY HYDROCARBON–ETHER AND HYDROCARBON–ALDEHYDE MIXTURES *

C. PANDO **, J.A.R. RENUNCIO **, R.W. HANKS and J.J. CHRISTENSEN

Department of Chemical Engineering and The Thermochemical Institute, Brigham Young University, Provo, UT 48602 (U.S.A.)

(Received 17 August 1982)

ABSTRACT

The method of Hanks, Gupta and Christensen for predicting vapor–liquid equilibria (VLE) from heat of mixing (h^E) data was applied to binary hydrocarbon–ether and hydrocarbon–aldehyde mixtures. Parameters for the Continuous Linear Association Model (CLAM) of Renon and Prausnitz were determined from h^E data measured at a temperature of 298.15 K for most of the mixtures. These parameters were used to predict VLE data at higher temperatures. It was not possible to evaluate parameters at the temperatures at which VLE data were measured because h^E data were not available at these temperatures. Nevertheless, the method seems to be able to account properly for the temperature dependence of VLE data. Results can be considered satisfactory given the large differences of temperature existing between the correlated VLE and h^E data.

INTRODUCTION

The prediction of vapor–liquid equilibrium (VLE) data for non-ideal mixtures has been the subject of numerous investigations [1,2]. Industrial processing very often occurs under conditions of temperature and pressure for which VLE data are not available. Designers of separation equipment are often faced with the task of either making new measurements or estimating the required data. Many estimation procedures have been proposed and used. The data required for their application and the accuracy of the predictions made vary considerably from one method to another.

Hanks et al. [3] have developed a procedure (here called the HGC method) in which excess enthalpy data, h^E, the Gibbs–Helmholtz equation, and a semi-empirical g^E model are used to predict VLE data for mixtures.

---

* Contribution No. 291 from The Thermochemical Institute.

** Permanent address: Departamento de Quimica Fisica, Universidad Complutense, Madrid-3, Spain.

This method provides for the simultaneous description of the excess free energy and excess enthalpy. The method requires no experimental VLE data, only excess enthalpies and pure component vapor pressure data. Generally predictions can be made with an error less than 10% in vapor phase mole fraction. This method has been shown to be successful in the calculation of both isothermal and isobaric VLE data for a variety of non-associating binary hydrocarbon mixtures and for associating alcohol–hydrocarbon mixtures [3–8]. Some multi-component mixtures have also been studied [4,5]. The method has also been shown to be capable of predicting VLE data at a higher temperature from lower temperature heat of mixing data provided that at least two sets of h^E data measured at different temperatures are available [5,7].

The purpose of the present paper is to extend the application of the HGC method to hydrocarbon–ether and hydrocarbon–aldehyde mixtures. h^E data for the mixtures considered have been taken from the literature. Unfortunately the h^E data were measured only at one temperature (usually 298.15 K) while VLE data were usually measured at temperatures considerably higher (333–383 K). Consequently, the ability of the method to perform temperature extrapolations when only one set of h^E data is available was severely tested.

PREDICTION METHOD

The usual approach to correlate VLE data for non-ideal mixtures is to measure total pressure–composition or vapor–liquid composition data from which liquid-phase activity coefficients may be calculated. The excess free energy is then computed from the activity coefficients and the resulting values are curve fitted to some semi-empirical model, $g^E(x_j, A_1, A_2 \ldots A_k)$ where x_j is the liquid mole fraction and A_k are adjustable parameters which are usually assumed to be temperature independent.

The correlation or prediction of other thermodynamic excess properties simultaneously with g^E is frequently attempted [9,10]. In order to predict h^E from g^E data, for instance, the semi-empirical equation for g^E has to be introduced in the Gibbs–Helmholtz relation

$$h^E = -T^2\, \partial(g^E/T)/\partial T \tag{1}$$

Results of such a prediction are usually poor unless the parameters of the g^E model are assumed to be temperature dependent [11], an approach which renders the equations so complex as to be of little practical use. When the model is able to simultaneously correlate g^E and h^E, an extremely accurate description of g^E is required due to the error magnification inherent in the differentiation process. If g^E data are required at another temperature T_1, different from that of the experimental data T_0, eqn. (1) has to be integrated graphically or numerically using actual h^E data in accordance with the relation

$$\frac{g^E(T_1)}{T_1} = \frac{g^E(T_0)}{T_0} - \int_{T_0}^{T_1} \frac{h^E(T)}{T^2}\, dT \tag{2}$$

Application of this equation requires a set of h^E data covering the temperature interval (T_0, T_1) for each mixture composition of interest. These data are usually not available for most systems.

The HGC method reverses the order of this process. The parameters A_k of the g^E model are evaluated by curve-fitting experimental binary isothermal h^E data to the algebraic equation $h^E(x_j, A_1, A_2 \ldots A_k)$ derived from the g^E model by application of eqn. (1). These A_k values are then used in the g^E model to calculate the activity coefficients from which the x–y data may be predicted.

For a great many systems the NRTL equation [1] has been found to be a useful model for g^E. However, when the HGC method was applied to hydrocarbon–alcohol mixtures, the CLAM equation [12] was shown to be required to adequately describe these associated solutions. Therefore, this latter model was used in the present study of hydrocarbon–ether and hydrocarbon–aldehyde mixtures in which appreciable chemical interactions also occur. According to this model, the equation for g^E is given by

$$g^E = \beta\phi_A\phi_B(x_A v_A + x_B v_B) + RT[x_A \ln(\phi_A/x_A) + x_B \ln(\phi_{B1}/\phi_{B1}^* x_B) + Kx_B(\phi_{B1} - \phi_{B1}^*)] \tag{3}$$

where ϕ_{B1} is

$$\phi_{B1} = \frac{1 + 2K\phi_B - (1 + 4K\phi_B)^{1/2}}{2K^2\phi_B} \tag{4}$$

An expression for ϕ_{B1}^* is obtained from eqn. (4) by setting $\phi_B = 1$. In these equations β is an adjustable physical interaction parameter (assumed to be temperature independent); $\phi_A = N_A/(N_A + \rho N_B)$ is the volume fraction of hydrocarbon solvent in solution; $\rho = v_B/v_A$ is the molar volume ratio of ether or aldehyde monomer to hydrocarbon; $\phi_B = 1 - \phi_A$ is the apparent volume fraction of ether or aldehyde; x_A and x_B are the apparent mole fractions of hydrocarbon and ether or aldehyde, respectively; and K is a chemical equilibrium constant for the association reaction

$$B_1 + B_n = B_{n+1} \tag{5}$$

where B_1 is the monomer and B_n is a polymer. The activity coefficients derived from eqn. (3) are given by [12]

$$\ln\gamma_A = \ln(\phi_A/x_A) + K\phi_A\phi_{B1}/\rho + \beta v_A\phi_B^2/RT + (\rho - 1)\phi_B/\rho \tag{6}$$

$$\ln\gamma_B = \ln(\phi_{B1}/\phi_{B1}^* x_B) + K(\phi_B\phi_{B1} - \phi_{B1}^*) + \beta v_B\phi_A^2/RT + (1 - \rho)\phi_A \tag{7}$$

When eqn. (1) is applied to eqn. (3), the algebraic expression for h^E is obtained

$$h^E = \beta\phi_A\phi_B(x_A v_A + x_B v_B) + \frac{x_B \Delta h^0}{2K\phi_B}\left[1 - \phi_B + \phi_B\sqrt{1+4K} - \sqrt{1+4K\phi_B}\right] \quad (8)$$

where $\Delta h^0 = T^2\ \partial(R\ \ln\ K)/\partial T$ is the enthalpy of hydrogen bond formation which was given the value −25,100 J mole^{-1} by Renon and Prausnitz [12].

In this paper eqn. (8) is curve fitted to the experimental h^E data using a non-linear regression method [13]. Both K and β are considered as adjustable parameters. The theoretical significance give to these parameters in the original formulation of the model would add an additional constraint to this semi-empirical solution theory. We have chosen to treat the CLAM equation as an effective semi-empirical curve-fitting form whose parameters have no physical significance. Nevertheless, some correlations between the values adopted by K and β and the type of system studied can be established, as will be discussed later. The values of K and β were used in eqns. (6) and (7) to compute activity coefficients. x–y values were then calculated by the usual method [1] assuming ideal vapor-phase behavior and also using Wilson's [14] formulation of the Redlich–Kwong equation.

RESULTS AND DISCUSSION

The Hanks–Gupta–Christensen method was applied to 12 hydrocarbon–ether and three hydrocarbon–aldehyde systems for which VLE and h^E data exist simultaneously in the literature. These systems are listed in Table 1 together with the source of data. Two more systems (benzene–diethyl ether and benzene–1,4 dioxane) were discarded because their heat of mixing data exhibit both an endothermic and an exothermic section and could not be fitted to eqn. (8). Two phase systems also were excluded.

Table 2 shows the temperature at which h^E data have been measured, the values of K and β, and the statistical measure of the fits (ratio of the h^E standard deviations σ to the maximum values of h^E). The conditions of the VLE data are also indicated in Table 2. When the data are isothermal, both the temperature and the range of total pressures are indicated. When the data are isobaric, the pressure and the temperature interval are stated. The mean deviation of y_A has been chosen as the criterion to examine the accuracy of the VLE predictions and is given in Table 2. Values for the maximum deviation are also reported in order to complement the information provided by the mean deviation. When experimental values of y_A were not available, the mean deviations of the total pressure were calculated and expressed in kPa. These results were obtained using the Redlich–Kwong equation of state for the vapor phase. However, results obtained when an ideal vapor-phase behavior is assumed are sufficiently close as to be consid-

TABLE 1

Binary systems studied and source of experimental data

System No.	Components		Refs.	
			h^E data	VLE data
I	*n*-Hexane (1)	1,4 Dioxane (2)	15	16, 17
II	*n*-Heptane (1)	Dipropyl ether (2)	18	19
III	*n*-Heptane (1)	Diisopropyl ether (2)	20	21
IV	*n*-Heptane (1)	Dibutyl ether (2)	18	22
V	*n*-Heptane (1)	1,4 Dioxane (2)	23	17
VI	*n*-Heptane (1)	Ethyleneglycol dimethyl ether (2)	18, 24	19
VII	Cyclohexane (1)	Propanal (2)	25	26
VIII	Cyclohexane (1)	Diethyl ether (2)	27	27
IX	Cyclohexane (1)	1,4 Dioxane (2)	28	29
X	Cyclohexane (1)	Furfural (2)	30	31
XI	Methylcyclohexane (1)	Furfural (2)	30	32
XII	Benzene (1)	Dipropyl ether (2)	24	33
XIII	Benzene (1)	Dimethoxymethane (2)	34,35	36
XIV	Benzene (1)	Ethyleneglycol dimethyl ether (2)	24	37
XV	Toluene (1)	1,4 Dioxane (2)	38	39, 40

ered adequate when a quick prediction is needed. Values for the molar volumes were taken from Timmermans [41] and from ref. 42. Some molar volumes had to be estimated using the method of Gunn and Yamada [43]. Application of Wilson's [14] formulation of the Redlich–Kwong equation requires the knowledge of the critical constants and accentric factors for pure components. Values for these parameters have been taken from Reid et al. [44]. Critical constants were estimated for a few components using the method of Lydersen [45]. When values for the accentric factor were not available, the procedure of Edmister [46] was used for their estimation. Values for the pure components vapor pressures were also taken from Reid et al. [44] except for the cases in which these values were reported together with total pressure measurements of the mixtures.

Since h^E data were only available at one temperature for each system, the temperature dependence of the parameters of the CLAM model [12] could not be determined. Values for the parameters K and β obtained from the lower temperature h^E data were used to calculate higher temperature VLE data. Nevertheless, the application of the HGC method [3] to this model leads to results which can be considered satisfactory given the large temperature extrapolations effected. Most systems have mean deviations in y_A ranging from 0.01 to 0.04. We note that values for the mean deviation

TABLE 2

Parameters for CLAM equation determined from h^E data and predictions of VLE data

System No.	h^E data (K)	K	β (J cm^{-3})	σ^a/h^E_{max} (%)	Type of VLE data	Predicted vapor composition	
						Mean deviation	Max. deviation
I	303.15	0.3861	9.02	2.5	353.15 K (61–140 kPa)	0.041	0.093
					101.35 kPa (342–358 K)	0.043	0.091
II	298.15	0.0420	0.53	1.8	343.15 K (42–52 kPa)	0.22 [b]	0.41 [b]
III	298.15	0.0182	3.67	0.2	101.35 kPa (342–363 K)	0.011	0.024
IV	298.15	0.0285	−1.23	4.6	363.15 K (26–77 kPa)	0.011	0.026
V	298.15	0.5167	1.03	4.6	353.15 K (53–59 kPa)	0.065	0.111
VI	298.15	0.2032	11.42	2.2	343.15 K (43–63 kPa)	0.012	0.022
VII	298.15	17.92	0.14	2.2	318.15 K (33–91 kPa)	0.028	0.085
VIII	298.15	0.1500	−8.30	1.2	298.15 K (22–65 kPa)	5.2 [b]	7.5 [b]
IX	348.15	0.3908	14.40	1.3	353.15 K (67–102 kPa)	2.0 [b]	2.9 [b]
X	348.15	1.1687	16.82	2.6	101.35 kPa (355–372 K)	0.024	0.081
XI	348.15	0.8392	14.63	4.2	101.35 kPa (374–393 K)	0.051	0.131
XII	298.15	0.0946	−6.73	3.5	323.15 K (25–35 kPa)	0.020	0.034
					333.15 K (38–51 kPa)	0.022	0.040
					343.15 K (55–73 kPa)	0.021	0.038
XIII	298.15	0.0247	−3.97	1.1	308.15 K (27–72 kPa)	0.017	−0.063
XIV	298.15	0.0100	−9.50	1.6	343.15 K (62–73 kPa)	4.0 [b]	6.0 [b]
XV	293.15	0.0545	−6.03	2.2	353.15 K (42–51 kPa)	0.020	−0.034
					373.15 K (80–97 kPa)	0.017	0.024
					26.66 kPa (335–341 K)	0.030	−0.054
					53.33 kPa (354–361 K)	0.028	−0.054
					101.35 kPa (374–383 K)	0.026	−0.051

[a] $\sigma = \sum_j (h_j^E, \text{calc.} - h_j^E, \text{exp.})^2/(N-3)^{1/2}$

[b] Mean deviation in the total pressure expressed in kPa.

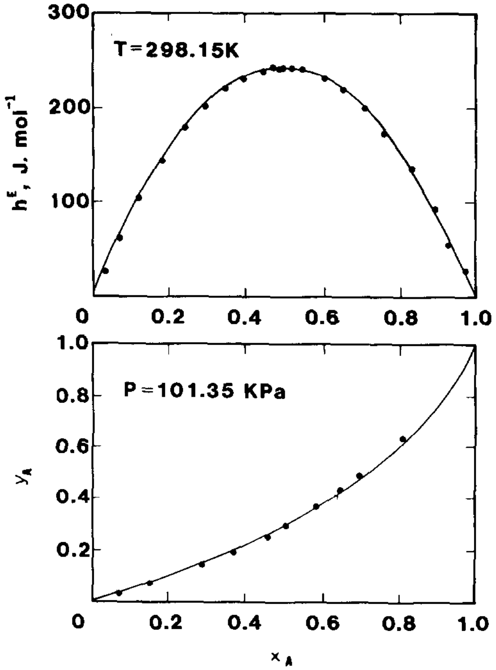

Fig. 1. Comparison of calculated and experimental data for the system *n*-heptane (1)+ diisopropyl ether (2). ●, Experimental; ———, calculated from the CLAM equation.

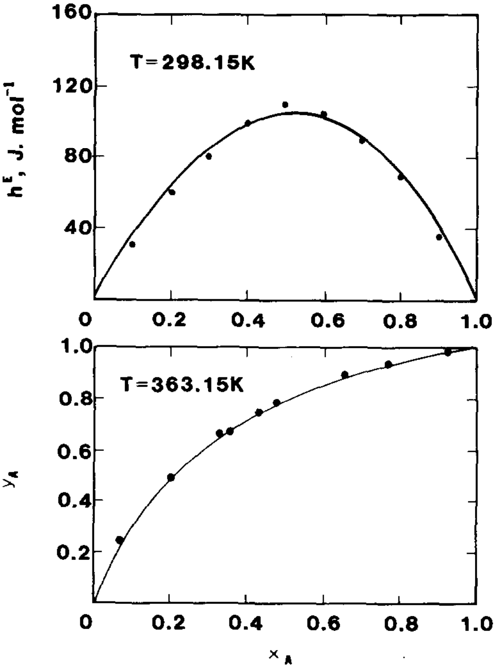

Fig. 2. Comparison of calculated and experimental data for the system *n*-heptane (1)+dibutyl ether (2). ●, Experimental; ———, calculated from the CLAM equation.

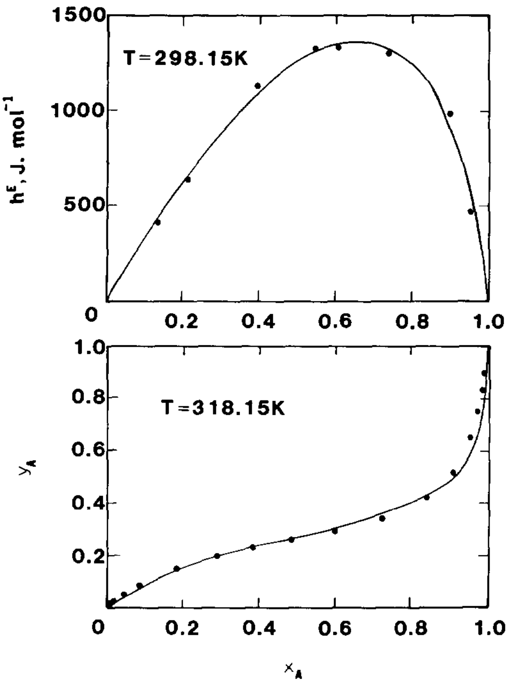

Fig. 3. Comparison of calculated and experimental data for the system cyclohexane (1)+ propanal (2). ●, Experimental; ———, calculated from the CLAM equation.

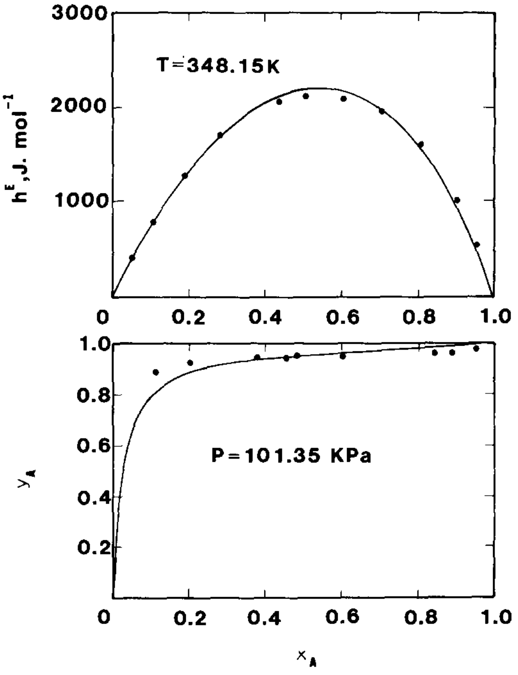

Fig. 4. Comparison of calculated and experimental data for the system cyclohexane (1)+ furfural (2). ●, Experimental; ———, calculated from the CLAM equation.

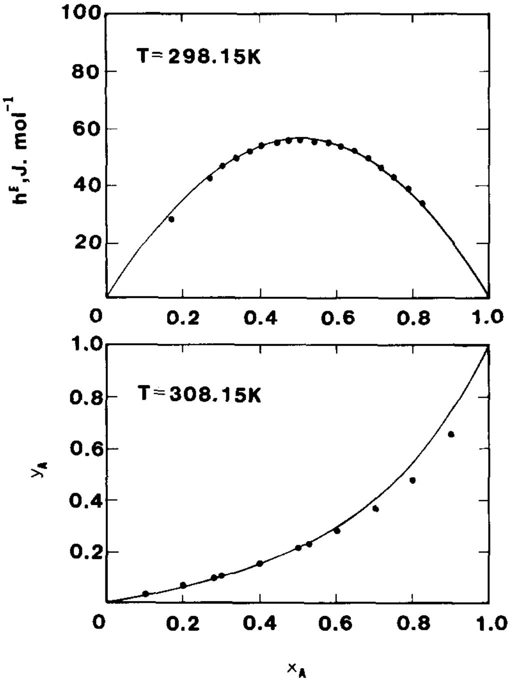

Fig. 5. Comparison of calculated and experimental data for the system benzene (1)+ dimethoxymethane (2). ●, Experimental; ————, calculated from the CLAM equation.

ranging from 0.01 to 0.03 are obtained when VLE data are directly fitted to an expression for g^E such as the Wilson, NRTL, UNIQUAC, etc. equations [47]. Thus, values of y_A predicted by the HGC method are essentially as accurate as experimental data. In order to examine the accuracy of the predictions when experimental values of y_A are not reported, values for the total pressure mean deviation should be compared with the corresponding pressure interval. Figures 1–5 show some typical examples of the results obtained, and correspond to systems comprised of an *n*-alkane, cycloalkane or aromatic hydrocarbon and an ether or aldehyde. The VLE data for these systems may be either isothermal or isobaric. These figs. indicate how the shape of the *x*–*y* curves varies considerably from one system to another.

We have unsuccessfully attempted to carry out calculations using eqn. (2) assuming that the heat of mixing does not vary appreciably with temperature. Values of g^E calculated this way differ largely from the values of g^E calculated from experimental data using Barker's method [48]. However, the assumption that h^E does not vary with temperature is equivalent to using the values of K and β obtained from h^E data at a lower temperature to estimate *x*–*y* data at a higher temperature. It seems that the HGC method used in conjunction with the CLAM model is able to account more properly for the temperature dependence of VLE data.

When the HGC method was applied previously to the CLAM equation in order to study hydrocarbon–alcohol systems, both K and β were also considered as adjustable parameters. The values found for K range from 8.5 to 707.5 and the values of β from -8.73 to 23.12 J cm^{-3} [8]. Correlations between the values assumed by the parameters and the nature of the components of the systems could not be established. Values of K for the hydrocarbon–ether and hydrocarbon–aldehyde systems are considerably lower (smaller than one in most cases). Values of β are similar to those obtained for the hydrocarbon–alcohol systems. If the physical significance attributed to the parameters in the original formulation of the CLAM model is taken into account, these changes in the values adopted by K and β seem to indicate that the physical interactions described by β are of similar magnitude for these systems, while the association reactions to which K is related are less important in the hydrocarbon–ether and hydrocarbon–aldehyde systems than in the hydrocarbon–alcohol systems.

CONCLUSIONS

The results of this study suggest that if h^E data for hydrocarbon–ether or hydrocarbon–aldehyde systems are available at only one temperature, both isothermal and isobaric VLE data at higher temperatures may be successfully estimated if the CLAM model is used in the Hanks–Gupta–Christensen method. The method is easy to use and typically VLE data 40–80 K higher than the h^E data can be predicted with essentially the same accuracy as the experimental data.

ACKNOWLEDGEMENTS

C. Pando wishes to acknowledge the Board of Foreign Scholarhsips and the Spanish Ministry of Education for their support through a Fulbright/MUI award.

REFERENCES

1 J.M. Prausnitz, Molecular Thermodynamics of Fluid-Phase Equilibria, Prentice Hall, Englewood Cliffs, NJ, 1969, Chaps. 6, 7.

2 J.M. Prausnitz, T. Anderson, E. Grens, C. Eckert, R. Hsieh and J. O'Connell, Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria, Prentice Hall, Englewood Cliffs, NJ, 1980.

3 R.W. Hanks, A.C. Gupta and J.J. Christensen, Ind. Eng. Chem., Fundam., 10 (1971) 504.

4 R.L. Tan, R.W. Hanks and J.J. Christensen, Thermochim. Acta, 21 (1977) 157.

5 R.L. Tan, R.W. Hanks and J.J. Christensen, Thermochim. Acta, 23 (1978) 29.

6 R.W. Hanks, R.L. Tan and J.J. Christensen, Thermochim. Acta, 23 (1978) 41.
7 R.W. Hanks, R.L. Tan and J.J. Christensen, Thermochim. Acta, 27 (1978) 9.
8 R.W. Hanks, T.K. O'Neill and J.J. Christensen, Ind. Eng. Chem., Process Des. Dev., 18 (1979) 408.
9 R.V. Orye, and J.M. Prausnitz, Indust. Eng. Chem., 57 (1965) 18.
10 D.J. Stookey, and B.D. Smith, Ind. Eng. Chem., Process Des. Dev., 12 (1973) 372.
11 L. Asselineau and H. Renon, Chem. Eng. Sci., 25 (1970) 1211.
12 H. Renon and J.M. Prausnitz, Chem. Eng. Sci., 22 (1967) 299; Errata, 22 (1967) 1891.
13 R.H. Pennington, Introductory Computer Methods and Numerical Analysis, Macmillan, London, 2nd edn., 1970.
14 G.M. Wilson, Adv. Cryog, Eng., 9 (1964) 168; 11 (1966) 392. 65th Natl. Meet., AIChE, 4–7 May, Cleveland 1969, Paper 15C.
15 M.D. Guillen and C. Gutierrez Losa, J. Chem. Thermodyn., 10 (1978) 567.
16 Y.S. Suryanarayana and M. Van Winkle, J. Chem. Eng. Data, 11 (1966) 7.
17 D. Tassios and M. Van Winkle, J. Chem. Eng. Data, 12 (1967) 555.
18 K. Sosnkowska-Kehiaian, R. Hryniewicz and H. Kehiaian, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 17 (1969) 185.
19 T. Treszczanowicz, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 21 (1972) 107.
20 M. Oba, S. Murakami and R. Fujishiro, J. Chem. Thermodyn., 9 (1977) 407.
21 S.V. Vijayaraghavan, P.K. Deshpande and N.R. Kuloor, J. Chem. Eng. Data, 12 (1967) 15.
22 V.C. Maripuri and G.A. Ratcliff, J. Chem. Eng. Data, 17 (1972) 454.
23 A. Inglese, E. Wilhem, J.P.E. Grolier and H.V. Kehiaian, J. Chem. Thermodyn., 12 (1980) 217.
24 H.V. Kehiaian, K. Sosnkowska-Kehiaian and R. Hryniewicz, J. Chim. Phys. Phys.-Chim. Biol., 68 (1971) 922.
25 B. Marongiu, H. Bros, M. Coten and H.V. Kehiaian, Int. Data Ser., Sel. Data Mixtures, Ser. A, (1974) 58. J. Chim. Phys. Phys.-Chim. Biol., 72 (1975) 378.
26 I. Matsunaga and T. Katayoma, J. Chem. Eng. Jpn., 6 (1973) 397.
27 H. Arm, D. Bankay, K. Strub and M. Wälti, Helv. Chim. Acta, 50 (1964) 1013.
28 A.W. Andrews and K.W. Morcom, J. Chem. Thermodyn., 3 (1971) 519.
29 H.W. Prengle and M.A. Pike, J. Chem. Eng. Data, 6 (1961) 400.
30 G.L. Nicolaides and C.A. Eckert, J. Chem. Eng. Data, 23 (1978) 152.
31 J.D. Thornton and F.H. Garner, J. Appl. Chem., Suppl., 1 (1951) 61.
32 F.H. Garner and R.T.W. Hall, J. Inst. Pet. London, 41 (1955) 373.
33 J. Linek, I. Wichterle and J. Polednova, Collect. Czech. Chem. Commun., 37 (1972) 2820.
34 R.J. Meyer, Int. Data Ser., Sel. Data Mixtures, Ser. A, (1977) 139.
35 F.J. Meyer and J.B. Metzger, Thermochim. Acta, 38 (1980) 197.
36 N.D. Litvinov, Zh. Fiz. Khim., 14 (1940) 782.
37 T. Treszczanowicz and H.W. Kehiaian, Int. Data Ser., Sel. Data Mixtures, Ser. A, (1975) 95.
38 P.P. Singh, R.C. Phutela and P.S. Arora, J. Chem. Soc., Faraday Trans. 1, 71 (1975) 1528.
39 Z. Gropsianu, J. Kyri and R. Gropsianu, Stud. Cercet. Stiintifici, Ser. Stiinte Chim., 4 (1957) 73.
40 M.P. Susarev and A.M. Toikka, Zh. Prikl. Khim. (Leningrad), 46 (1973) 2461.
41 J. Timmermans, Physico-chemical Constants of Pure Organic Compounds, Elsevier, Amsterdam, Vol. 1 (1950); Vol. 2 (1965).
42 Handbook for Chemistry and Physics, CRC Press, Cleveland, OH, 56th edn., 1975–1976.
43 R.D. Gunn and T. Yamada, AIChE J., 17 (1971) 1341.
44 R.C. Reid, J.M. Prausnitz and T.K. Sherwood, The Properties of Gases and Liquids, McGraw-Hill, New York, NY, 3rd edn., 1977, p. 629.

45 A.L. Lydersen, Univ. Wis. Eng. Exp. Stn. Rep., 3 (1955).
46 W.C. Edmister, Pet. Refiner, 37 (1958) 173.
47 J. Gmehling and U. Onken, Vapor–Liquid Equilibrium Data Collection, Chemistry Data Series, Dechema, Frankfurt, 1977.
48 J.A. Barker, Aust. J. Chem., 6 (1953) 207.