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Literature Cited

- (1) Rao, Y. P.; Suri, S. K. *Thermochim. Acta* **1980**, *36*, 243.
- (2) Suri, S. K.; Ramakrishna, V. J. *Chem. Thermodyn.* **1975**, *7*, 573.
- (3) Suri, S. K.; Maheswari, R. C.; Yadav, P. L. *Indian J. Chem.* **1974**, *12*, 620.

- (4) Riddick, J. A.; Bunger, W. B., Eds. "Technique of Organic Chemistry", 3rd ed.; Wiley-Interscience: New York, 1970; Vol. II.
- (5) Hepler, L. G.; Fenby, D. V. *J. Chem. Thermodyn.* **1973**, *5*, 471.
- (6) American Petroleum Institute Research Project 44, Chemical Thermodynamics Properties Center, Texas A & M University, College Station, TX (Tables dated April 30, 1977, and April 30, 1956).
- (7) Letcher, T. M.; Bayles, J. W. *J. Chem. Eng. Data* **1971**, *16*, 266.
- (8) Spencer, C. F.; Adler, S. B. *J. Chem. Eng. Data* **1978**, *23*, 82.
- (9) Maheswari, R. C.; Suri, S. K.; Tewari, U. S. *J. Chem. Eng. Data* **1979**, *24*, 237.
- (10) Letcher, T. M. *J. Chem. Thermodyn.* **1972**, *4*, 159.

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Thermodynamic Properties of Solutions Containing an Aliphatic Amine. 2. Excess Volumes of Binary Mixtures of Triethylamine with 12 Hydrocarbons at 313.15 K

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Molar excess volumes of binary mixtures of triethylamine with *n*-propylbenzenes, isopropylbenzene, 1,3,5-trimethylbenzene, 1,2,3,4-tetramethylbenzene, diphenylmethane, *n*-hexane, *n*-octane, 2,2,4-trimethylpentane, *n*-dodecane, 2,2,4,6,6-pentamethylheptane, cyclohexane, and methylcyclohexane at 313.15 K have been calculated from the experimental density data. The variation of V^E with the change in size, substitution, and molecular geometry of the hydrocarbon has been discussed.

Introduction

In part 1 (1) we reported molar excess volumes for the binary mixtures of triethylamine with benzene, toluene, ethylbenzene, and the three isomeric xylenes. As an extension of that work, we have determined the excess volumes for the mixtures of triethylamine with *n*-propylbenzene, isopropylbenzene, 1,3,5-trimethylbenzene, 1,2,3,4-tetramethylbenzene, diphenylmethane, *n*-hexane, *n*-octane, 2,2,4-trimethylpentane, *n*-dodecane, 2,2,4,6,6-pentamethylheptane, cyclohexane, and methylcyclohexane. The purpose of these investigations is to provide some information about the thermodynamic properties of amine-hydrocarbon mixtures with a view to understanding the factors determining the unlike interactions between the molecules in such mixtures.

Experimental Section

The sample of triethylamine supplied by Fisher was purified by following the procedure used by Hepler and Fenby (2). ACS certified grade *n*-hexane, *n*-octane, and cyclohexane supplied by Fisher, IR and GC analyzed grade *n*-dodecane and methylcyclohexane and puriss grade 1,3,5-trimethylbenzene supplied by Aldrich, reagent grade isopropylbenzene supplied by Eastman, and Baker analyzed reagent grade 2,2,4-trimethylpentane were purified according to standard procedures (3). *n*-Propylbenzene and 1,2,3,4-tetramethylbenzene (both IR and GC analyzed grade) and puriss grade 2,2,4,6,6-pentamethylheptane supplied by Aldrich were fractionally distilled at a reflux ratio of 1:10, and

Table I. Densities and Refractive Indexes of Liquids Used

liquid	density at 313.15 K		refractive index at 298.15 K	
	our value	lit. value (6)	our value	lit. value (6)
triethylamine	0.709 32	0.7092 ^a	1.3978	1.3980 ^a
<i>n</i> -propylbenzene	0.845 08	0.8454	1.4895	1.489 51
isopropylbenzene	0.844 67	0.8447	1.4888	1.488 90
1,3,5-trimethylbenzene	0.848 90	0.8488	1.4969	1.496 84
1,2,3,4-tetramethylbenzene	0.887 84	0.9015 ^b	1.5182	1.518 1
diphenylmethane	0.989 92	1.0020 ^b		
<i>n</i> -hexane	0.641 09	0.6409	1.3722	1.372 26
<i>n</i> -octane	0.686 56	0.6863	1.3952	1.395 05
2,2,4-trimethylpentane	0.675 29	0.6754	1.3888	1.388 98
<i>n</i> -dodecane	0.734 57	0.7344	1.4194	1.419 52
2,2,4,6,6-pentamethylheptane	0.731 5	0.7417 ^b	1.4167	1.416 7
cyclohexane	0.759 67	0.7598	1.4234	1.423 54
methylcyclohexane	0.751 99	0.7520	1.4204	1.420 58

^a From ref 1. ^b Density at 298.15 K.

the middle fraction was collected. Reagent grade diphenylmethane supplied by Eastman was purified by cycles of fractional crystallization. It was finally distilled under reduced pressure. All of the reagents were stored in brown bottles and fractionally distilled immediately before use. The densities and refractive indexes of the solvents have been compared with the accepted literature values (4) in Table I.

The molar excess volumes of mixing have been calculated from the experimental density data. The solutions for the measurement of densities were prepared by weight, and corrections for buoyancy were applied. The details of the experimental technique for the preparation of solutions have been described earlier (5).

The densities were measured with a vibrating flow densimeter (Sodev, Inc.). The liquids flowed (at a flow rate of ~ 0.5 cm³·min⁻¹) through the densimeter under positive pressure. Water from a thermostat was circulated through the densimeter module at a flow rate of $\sim 2-3$ L·min⁻¹. The temperature of the thermostat (313.15 K) was maintained at ± 0.001 K by using

Table II. Excess Volumes of Mixing, V^E ($\text{cm}^3\cdot\text{mol}^{-1}$), for the Binary Mixtures at 313.15 K

X_1	V^E	X_1	V^E	X_1	V^E	X_1	V^E
Triethylamine (1) + <i>n</i> -Propylbenzene (2)				Triethylamine (1) + <i>n</i> -Octane			
0.1460	-0.243	0.5086	-0.483	0.0926	0.028	0.5406	0.093
0.1764	-0.287	0.5858	-0.466	0.1667	0.057	0.6035	0.081
0.3533	-0.435	0.6787	-0.435	0.2604	0.074	0.7345	0.076
0.4157	-0.461	0.8197	-0.306	0.3639	0.095	0.7876	0.066
0.4948	-0.488	0.9165	-0.169	0.4572	0.094	0.8762	0.051
Triethylamine (1) + Isopropylbenzene (2)				Triethylamine (1) + 2,2,4-Trimethylpentane			
0.0881	-0.122	0.6173	-0.475	0.0982	0.007	0.6395	0.031
0.1582	-0.198	0.6787	-0.468	0.1633	0.002	0.7308	0.034
0.2667	-0.303	0.7686	-0.426	0.2416	0.013	0.7905	0.031
0.3307	-0.360	0.8512	-0.347	0.3618	0.014	0.8612	0.029
0.4692	-0.453	0.9257	-0.203	0.4289	0.028	0.9334	0.020
0.5262	-0.467			0.5452	0.031		
Triethylamine (1) + 1,3,5-Trimethylbenzene				Triethylamine (1) + <i>n</i> -Dodecane			
0.0854	-0.082	0.4951	-0.353	0.1326	0.063	0.6314	0.097
0.1729	-0.148	0.6131	-0.385	0.2829	0.104	0.6988	0.084
0.1831	-0.154	0.7080	-0.345	0.3314	0.118	0.7962	0.072
0.2583	-0.209	0.8156	-0.258	0.4509	0.121	0.8966	0.049
0.3427	-0.262	0.8910	-0.166	0.5100	0.114		
0.4181	-0.322			Triethylamine (1) + 2,2,4,6,6-Pentamethylheptane			
Triethylamine (1) + 1,2,3,4-Tetramethylbenzene (2)				0.1271	0.048	0.5934	0.066
0.0914	-0.183	0.5914	-0.707	0.1873	0.064	0.7061	0.050
0.1975	-0.378	0.6884	-0.635	0.3748	0.077	0.8222	0.029
0.2589	-0.488	0.7854	-0.485	0.5195	0.075	0.9327	0.008
0.3428	-0.601	0.8512	-0.348	Triethylamine (1) + Cyclohexane (2)			
0.4248	-0.684	0.9146	-0.208	0.1274	0.093	0.5352	0.183
0.5029	-0.714			0.2074	0.147	0.6233	0.156
Triethylamine (1) + Diphenylmethane (2)				0.2840	0.194	0.6954	0.141
0.0947	-0.475	0.5372	-1.352	0.3661	0.212	0.7952	0.109
0.2001	-0.810	0.6673	-1.304	0.4232	0.208	0.9011	0.064
0.2918	-1.024	0.7875	-1.006	Triethylamine (1) + Methylcyclohexane (2)			
0.3710	-1.174	0.9055	-0.496	0.1575	-0.048	0.5435	-0.101
0.4407	-1.273			0.2335	-0.060	0.6100	-0.089
Triethylamine (1) + <i>n</i> -Hexane (2)				0.3213	-0.076	0.6932	-0.076
0.1108	0.017	0.4932	0.052	0.3742	-0.087	0.7978	-0.047
0.1939	0.025	0.6398	0.048	0.4754	-0.096		
0.3234	0.041	0.7919	0.036				
0.3994	0.054	0.9233	0.017				

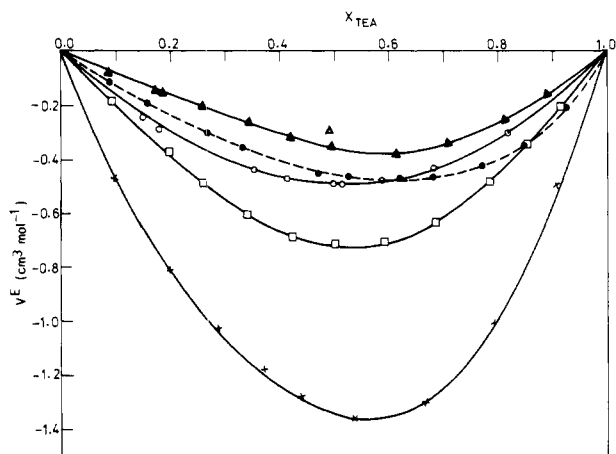


Figure 1. Molar excess volumes of mixing at 313.15 K for the binary mixtures of triethylamine (TEA) + *n*-propylbenzene (O); + isopropylbenzene (●); + 1,3,5-trimethylbenzene (▲); + 1,2,3,4-tetramethylbenzene (□); and + diphenylmethane (X). (Δ) Literature value (ref 9) for TEA + 1,3,5-trimethylbenzene at 298.15 K.

a Tronac precision temperature controller. The densimeter was calibrated with nitrogen gas and degassed ion-exchanged water by using the densities of Kell (δ). Duplicate densities of liquids and liquid mixtures studied agreed within $1 \times 10^{-5} \text{ g}\cdot\text{cm}^{-3}$. An analysis of the experimental uncertainties led to the conclusion that the reported excess volumes of mixing were within $\pm 0.005 \text{ cm}^3\cdot\text{mol}^{-1}$ as can be judged by the standard deviations given in Table III.

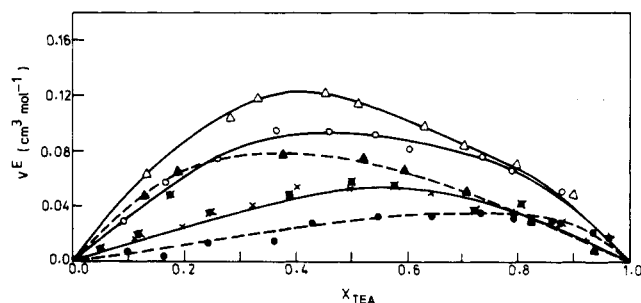


Figure 2. Molar excess volumes of mixing at 313.15 K for the binary mixtures of triethylamine (TEA) + *n*-hexane (X); + *n*-octane (O); + 2,2,4-trimethylpentane (●); + *n*-dodecane (Δ); and + 2,2,4,6,6-pentamethylheptane (▲). (⊗) Literature value (ref 7) for TEA + *n*-hexane at 298.15 K.

Results and Discussion

The molar excess volumes of mixing, V^E , for the binary mixtures at 313.15 K are recorded in Table II, and a graphical representation is given in Figures 1–3. The data were fitted to a smoothing equation of the type

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1(1-x_1)[A + B(2x_1-1) + C(2x_1-1)^2 + D(2x_1-1)^3] \quad (1)$$

where x_1 refers to the mole fraction of triethylamine. Values of the parameters A , B , C , and D and the standard deviation for the excess volumes, $\sigma(V^E)$, are given in Table III.

The literature values for the binary mixtures of triethylamine with hexane (7), cyclohexane (7), methylcyclohexane (8), and

Table III. Parameters of Eq 1 and Standard Deviation $\sigma(V^E)$ of Experimental Values at 313.15 K

system 1 + 2	parameters of eq 1				std dev $\sigma(V^E)$, $\text{cm}^3 \cdot \text{mol}^{-1}$
	A	B	C	D	
triethylamine + <i>n</i> -propylbenzene	-1.9248	-0.080	-0.226	-0.106	0.004
triethylamine + isopropylbenzene	-1.8264	-0.719	-0.529	-0.267	0.005
triethylamine + 1,3,5-trimethylbenzene	-1.4318	-0.796	0.131	0.624	0.004
triethylamine + 1,2,3,4-tetramethylbenzene	-2.8722	-0.451	0.643	0.237	0.003
triethylamine + diphenylmethane	-5.3447	-1.536	-0.557	2.035	0.004
triethylamine + <i>n</i> -hexane	0.2118	0.013	-0.042	0.064	0.002
triethylamine + <i>n</i> -octane	0.3673	-0.127	0.137	0.427	0.004
triethylamine + 2,2,4-trimethylpentane	0.1013	0.115	0.072	0.056	0.003
triethylamine + <i>n</i> -dodecane	0.4541	-0.205	0.068	0.339	0.004
triethylamine + 2,2,4,6,6-pentamethylheptane	0.3006	-0.116	0.031	-0.130	0.003
triethylamine + cyclohexane	0.7895	-0.440	-0.015	0.620	0.004
triethylamine + methylcyclohexane	-0.4019	-0.072	0.255	0.388	0.003

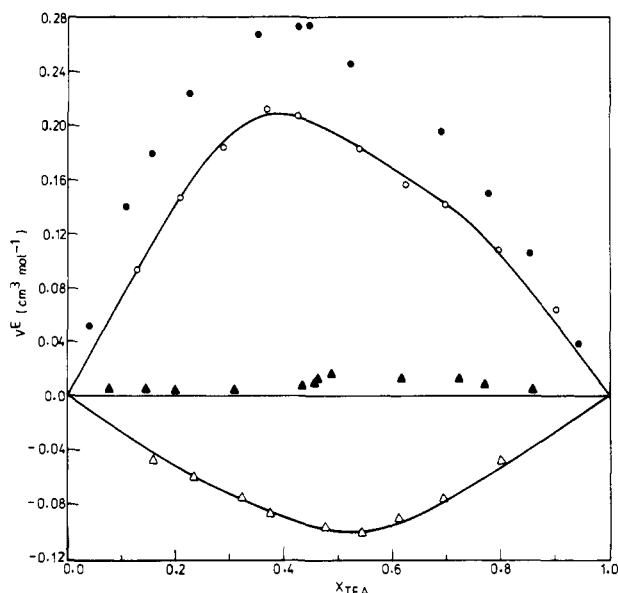


Figure 3. Molar excess volumes of mixing at 313.15 K for the binary mixtures of triethylamine (TEA) + cyclohexane (O); + methylcyclohexane (Δ). Solid points indicate Letcher's values (ref 7 and 8) at 298.15 K.

1,3,5-trimethylbenzene (9) all reported at 298.15 K have been compared with our values at 313.15 K in Figures 1-3. To the best of our knowledge no V^E data have been reported in the literature for other binary mixtures reported here.

In Figure 4, excess volumes at equimolar concentration, $V_{0.5}^E$, have been plotted as a function of number of carbon atoms in the hydrocarbon. A plot of $V_{0.5}^E$ vs. molar volume of the hydrocarbon yields a similar plot.

The unlike interactions between the lone pair of electrons of the N atom (rather than the C-N bond dipole) of triethylamine with the easily polarizable π electrons of benzene have already been established (1, 10, 11). The methyl substitution in cyclohexane or benzene produces structural changes in the hydrocarbon and, in the case of benzene, a weakening of the like π - π interactions resulting in increased unlike n - π interactions. A comparison of the first part of curve D and curve A of Figure 4 suggests that the volumetric effects caused by structural changes predominate over the change in n - π interactions caused by alkyl substitution. The increase in the length of the substituent alkyl group makes the molecule more polarizable and hence more strongly interacting (curve D, Figure 4). These n - π interactions produce an increasingly more negative V^E when the number of methyl substituents increases. The volumetric effects are less negative when the methyl substitutions are at the meta position (curve C, Figure 4) as compared to those at

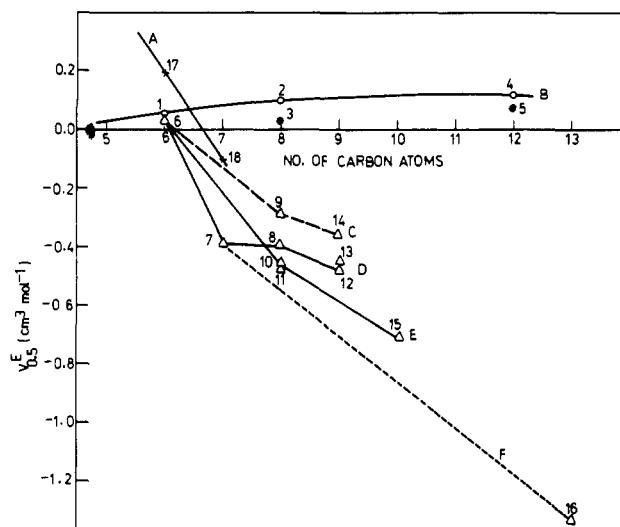


Figure 4. Excess volumes at equimolar concentration, $V_{0.5}^E$ at 313.15 K plotted against the number of carbon atoms in the hydrocarbon: (1) *n*-hexane; (2) *n*-octane; (3) 2,2,4-trimethylpentane; (4) *n*-dodecane; (5) 2,2,4,6,6-pentamethylheptane; (6) benzene (1); (7) toluene (1); (8) ethylbenzene (1); (9) *m*-xylene (1); (10) *o*-xylene (1); (11) *p*-xylene (1); (12) *n*-propylbenzene; (13) isopropylbenzene; (14) 1,3,5-trimethylbenzene; (15) 1,2,3,4-tetramethylbenzene; (16) diphenylmethane; (17) cyclohexane; and (18) methylcyclohexane.

the ortho position (curve E, Figure 4). Diphenylmethane, because of the large aromatic proportion in the molecule, offers appreciable volumetric effects (curve F, Figure 4).

The binary mixtures of triethylamine with *n*-alkanes show small positive excess volumes. The magnitude of $V_{0.5}^E$ in these solutions increases initially with the number of carbon atoms in the hydrocarbon but has a tendency to reach an optimum value (curve B, Figure 4). It is interesting to observe that the solutions containing methyl-substituted structural isomers exhibit smaller $V_{0.5}^E$ values than those containing *n*-alkanes. The excess volumes for solutions of 2,2,4-trimethylpentane and 2,2,4,6,6-pentamethylheptane are of the same order of magnitude as one would expect for *n*-pentane and *n*-heptane, respectively (from curve B of Figure 4). It appears that the volumetric effects in these solutions are determined by the length of the chain of the alkane molecule and the number of methyl substitutions in the molecule play an almost insignificant role.

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Literature Cited

- (1) Rao, Y. P.; Suri, S. K. *J. Chem. Eng. Data*, preceding paper.
- (2) Hepler, L. G.; Fenby, D. V. *J. Chem. Thermodyn.* 1973, 5, 471.
- (3) Riddick, J. A.; Bunger, W. B., Eds. "Technique of Organic Chemistry", 3rd ed.; Wiley-Interscience: New York, 1970; Vol. II.
- (4) American Petroleum Institute Research Project 44, Chemical Thermodynamics Properties Center, Texas A & M University, College Station, TX.
- (5) Maheshwari, R. C.; Suri, S. K.; Tewari, U. S. *J. Chem. Eng. Data* 1979, 24, 237.
- (6) Keil, G. S. *J. Chem. Eng. Data* 1970, 15, 119.
- (7) Letcher, T. M. *J. Chem. Thermodyn.* 1972, 4, 159.
- (8) Letcher, T. M. *J. Chem. Thermodyn.* 1972, 4, 551.
- (9) Kohlar, F.; Rott, E. *Monatsh. Chem.* 1954, 85, 703.
- (10) Letcher, T. M.; Bayles, J. W. *J. Chem. Eng. Data* 1971, 16, 266.
- (11) Kahialan, H. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* 1966, 14, 703.

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Ternary Vapor-Liquid Equilibria at 760 mmHg in the Systems Methanol-Diethyl Ketone-Methyl Isobutyl Ketone and Methanol-Methyl Ethyl Ketone-Methyl Isobutyl Ketone

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The vapor-liquid equilibria for the ternary systems methanol-diethyl ketone-methyl isobutyl ketone and methanol-methyl ethyl ketone-methyl isobutyl ketone were determined at 760 mmHg by using a Dvorak and Boublik recirculation still. The data were correlated by means of the Wilson and Redlich-Kister equations and by an equation based on the separation factor. Direct correlation of the ternary data without considering binary data was found very efficient. The prediction of the binary and ternary data by the UNIFAC method was good. Boiling points of the ternary mixtures were predicted by an empirical correlation within a mean error of $\pm 1.0\%$.

The aim of the present study was to establish new vapor-liquid equilibria data at 760 mmHg for the ternary systems methanol-diethyl ketone (DEK)-methyl isobutyl ketone (MIBK) and methanol-methyl ethyl ketone (MEK)-MIBK and to check the possibility for their prediction from available binary data and by the UNIFAC method (5). The possibility and the advantage of direct correlation of the ternary data without considering the binary data was also checked as well as various equations for correlating the data.

The following binary data were employed: for DEK-MIBK and MEK-MIBK the data of Wisniak and Tamir (1), for methanol-DEK the data of Glukhareva et al. (3), for methanol-MEK and for methanol-MIBK the data of Eduljee and Tiwari (4). It should be noted that the data of Hill and Van Winkle (2) for methanol-MIBK were found by Eduljee and Tiwari (4) incorrect because of errors in the measurements of the boiling temperature of the mixtures and vapor pressure data. In addition the conversion of mass fractions to mole fractions is in error.

Analytical grade reagents purchased from Merck were used. The physical properties of the pure components (refractive index and boiling point) appeared in ref 1, and the properties of methanol agreed with literature data. The equilibrium determinations were made in a modified all-glass Dvorak and Boublik recirculation still (6), and the experimental features have been described previously (7). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and an Autolab Minigrator type of electronic integrator. For methanol-DEK-MIBK the chromatographic column was packed with Poropak Q (20%) and operated isothermally at 245 °C. The injector temperature was 340 °C, and the detector was operated at 150

mA and 340 °C. For methanol-MEK-MIBK the column was packed with Chromosorb 101 and operated at 175 °C. Other operating conditions are similar. Concentration measurements in both cases were generally accurate to ± 0.004 mole fraction.

Treatment of the Data

The correlation of ternary data by a series expansion of the Redlich-Kister type is usually based on the binary data; the ternary data are used to compute the so-called ternary constant. The magnitude of this constant also gives an indication of whether it is possible to predict the ternary data from the binaries alone. When handling multicomponent data it is possible to avoid complex equations and a large number of adjustable variables by direct correlation of the available information, without consideration of lower order data (namely the binary data in the case of ternary mixtures or binary and ternary data in the case of quaternary mixtures, etc.) It has been shown elsewhere (8) that direct correlation can be more efficient for the following arguments: (1) fewer parameters are needed in the correlated equations for the same degree of the fit of data and (2) for an identical number of parameters, the goodness of the fit is better by means of direct correlation of the multicomponent data. The above conclusions will be demonstrated here since the binary data are available.

The following equations were used for correlating the multicomponent vapor-liquid equilibria data:

(a) An equation which relates the boiling temperature of the mixture with the liquid composition solely has been derived (8) on the basis of the concept of "excess property", and it reads

$$T = \sum_{i=1}^N x_i T_i^0 + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + \dots] \quad (1)$$

This equation is useful for obtaining isothermals and for exploring the azeotropic behavior and distillation paths of ternary mixtures. For binary mixtures the second summation on the right-hand side of eq 1 is exactly that suggested by Redlich and Kister (17). For multicomponent mixtures, we kept the binary form of the Redlich and Kister equation, but the significance of the equation is different from that suggested by them in the sense that coefficients A_{ij} , B_{ij} , etc., are not binary constants; namely, they are not determined from the binary data. These coefficients are