A Modification of Regular Solution Theory to Incorporate an Improved Approximation for Pair Distribution Functions in Mixtures

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The radial distribution functions for pairs in a fluid mixture can be closely approximated from known data on pair distribution functions for pure components evaluated at a mean density determined by a properly defined average of molecular interaction parameters in the mixtures. This approximation has been used to replace the assumption about structure in mixtures inherent in the traditional regular solution theory. The result is a modified regular solution theory which gives an improvement in predicting excess thermodynamic functions and activity coefficients in mixtures involving appreciable differences in molecular size and shape.

SCOPE

This study was conducted to investigate the usefulness of some new theoretical knowledge about the structure of fluid mixtures. The term structure in mixtures of simple fluids means a description of the probability of finding the center of one molecule at various distances from the center of another and the probability that the molecules found at a given separation belong to various species among those present in the mixture.

This new theoretical development was used to improve the description of structure inherent in the Hildebrand regular solution theory using solubility parameters. The simplicity of this theory has made it attractive for engineering computations, but, in its original form, it was quite limited in its range of applicability. One of the early improvements in the theory was the incorporation of the Flory-Huggins equation for the entropy of mixing to replace the ideal solution entropy of mixing assumed by the original theory.

This work is an attempt to make another improvement in this theory by improving one of the basic assumptions while retaining as much as possible its simplicity. The objective is to remove the unrealistic assumption in the original theory that the probability of a particular pair of molecules having a specified center-to-center separation distance in the mixture is independent of composition and is exactly the same as that of the pair in a pure component at the temperature and pressure of the mixture.

The correct pair distribution function in a mixture of dissimilar molecules, however, is very much composition dependent, and the improvement here accounts for this dependence by means of an assumption called the mean density approximation. The effectiveness of this approximation is demonstrated in this paper by comparison of pair distribution functions in an ideal mixture of Lennard-Jones fluids calculated by this procedure with those obtained from computer simulations of this mixture.

The new approximation was incorporated into the regular solution theory and tested by making excess free energy calculations in real binary mixtures with varying degrees of dissimilarity of molecular size and character.

CONCLUSIONS AND SIGNIFICANCE

The results for the new modified regular solution theory (MRST) show in every case an improvement in calculated values of the excess Gibbs free energy and excess enthalpy of mixtures when the molecules in the mixture differ appreciably in size. For molecules of approximately the same size, the modified theory gives essentially the same results as the traditional regular solution theory.

The results lend support to the conclusion that the regular solution theory does not derive its success from a cancellation of errors but that it is based on a well-defined model with correctly assessed assumptions, so that better results follow the improvement of any one of them.

It should be pointed out, however, that in any mixture theory the most important single assumption to be made in the calculation of excess functions is that concerning the unlike pair interactions. Small errors in predicting this contribution can completely offset any improvement derived from the better description of the fluid structure. However, if the unlike pair interaction is determined from a single data point at one composition, as in this study, then the structural improvement proposed is definitely worthwhile in predicting results at other compositions.

After uncertainties in the unlike pair contribution are eliminated by fitting to a single data point, this study has dealt with only one of the remaining basic assumptions of the regular solution theory, that concerning structure. No change at all was made in the assumptions of negligible volume change on mixing and that the entropy of mixing is athermal and represented by the Flory-Huggins equation. Consequently, this study has not produced a theory which is necessarily adequate for all mixtures, regardless of molecular type. It has been the purpose here to show that this improvement in the description of the structure of a mixture is definitely worthwhile and should be incorporated not only into regular solution theory but into others with a theoretical base.

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The radial distribution function for an α, β pair in a mixture $g_{\alpha\beta}(r)$ is proportional to the probability that a molecule of species α is at a distance r from one of species β and plays an important role in the understanding of physical properties of fluid mixtures. Examples of such properties are configurational and residual thermodynamic functions (internal energy, pressure, isothermal compressibility, etc.), the shift in bond vibration frequencies with density or solvent, and the scattering cross section for light or neutrons (O'Connell, 1971; Egelstaff, 1967).

A model to predict the radial distribution function in mixtures from those of the pure components using a suitably defined mean density was proposed in previous studies by Fisher and Leland (1970) and Mansoori and Leland (1972). The model is tested by comparing the results for g_{AK} with those obtained by molecular dynamics calculations for argon-krypton liquid mixtures. Applications of this model include the formulation of a modified regular solution theory (MRST) which enables one to compute, among other things, the excess Gibbs free energy, the activity coefficients, vapor pressures, and the excess enthalpy of mixing.

THE MEAN DENSITY APPROXIMATION

The radial distribution function g^0_{11} in a pure fluid consisting of type 1 molecules is given by

$$g^0_{11} = g^0_{11}\left(\frac{r}{\sigma_{11}}, \frac{\epsilon_{11}}{kT}, \rho\sigma^3_{11}\right) \qquad (1)$$

We propose to show that in a mixture of type 1 and type 2 molecules, the radial distribution function g^M_{11} is given to a good approximation by the relation

$$g^M_{11} \cong g^0_{11}\left[\frac{r}{\sigma_{11}}, \frac{\epsilon_{11}}{kT}, \rho_M(\bar{\sigma})^3\right] \qquad (2)$$

Equation (2) is called the mean density approximation in which

$$(\bar{\sigma})^3 = \sigma^3_{11}x_1^2 + 2\sigma^3_{12}x_1x_2 + \sigma^3_{22}x_2^2 \qquad (3)$$

Ideally, one should use $\sigma_{12} = \lambda(\sigma_1 + \sigma_2)/2$ in Equation (3), where λ is a correction factor usually slightly greater than unity. However, values of λ are not well known. In this case, the mean density approximation in Equation (2) for pairs with large size differences give best results with the definition

$$\sigma^3_{12} = \frac{(\sigma_1^3 + \sigma_2^3)}{2} \qquad (4)$$

An explanation of the mean density approximation in Equation (2) may be obtained from an examination of the role of the $\rho\sigma^3$ term in the distribution function for a pure component as given by Equation (1). At low densities, where the fluid may be described by a virial expansion truncated after the second virial, the distribution function has the limit

$$\lim_{\rho\to 0} g(r) = \exp\left[\frac{-\epsilon}{kT} f\left(\frac{r}{\sigma}\right)\right]$$

which is completely independent of density. In this second virial limit, the $g(r)$ function is that due to a pair interaction entirely uninfluenced by neighbouring molecules. At higher densities, the $\rho\sigma^3$ term then accounts for the effect of the environment around the pair produced by its neighbors. The approximation in Equation (2) is that in a mixture this environmental effect can be described by a fluid whose density depends on the composition of the mixture. The $(\bar{\sigma})^3$ term in the van der Waals one-fluid theory is precisely the parameter which plays this role in representing a mixture environment around a pair in terms of a pure component reference.

Table 1. Comparison of the Radial Distribution Function g_{AA} Using the Mean Density Approximation (MDA) with Molecular Dynamics Results of Mo et al. (1974) for Argon-Krypton Mixture ($x_A = 0.1$) at 116°K

r/σ_{AA}	g^M_{AA} (mole dynamics)	g^0_{AA} (MDA)
1.01	1.20	1.25
1.05	2.62	2.48
1.09	2.71	2.65
1.12	2.40	2.49
1.17	2.07	2.05
1.23	1.45	1.47
1.29	1.10	1.09
1.33	0.88	0.92
1.41	0.72	0.72
1.45	0.63	0.65
1.49	0.60	0.63
1.52	0.55	0.61
1.59	0.60	0.63

Table 2. Comparison of the Radial Distribution Function g_{KK} Using the Mean Density Approximation (MDA) with the Molecular Dynamics Results of Mo et al. (1974) for Argon-Krypton Mixture ($x_A = 0.5$) at 116°K

r/σ_{KK}	g^M_{KK} (mole dynamics)	g^0_{KK} (MDA)
1.02	1.67	1.59
1.05	2.64	2.45
1.07	2.82	2.77
1.12	2.80	2.92
1.15	2.40	2.55
1.19	1.98	2.10
1.20	1.76	1.93
1.24	1.42	1.55
1.26	1.30	1.40
1.30	1.09	1.13
1.32	1.00	1.05
1.36	0.88	0.89
1.43	0.69	0.72

Table 3. Comparison of the Radial Distribution Function g_{AK} Using the Mean Density Approximation (MDA) with Molecular Dynamics Results of Mo et al. (1974) for Argon-Krypton Mixture ($x_A = 0.9$) at 116°K

r/σ_{AK}	g^M_{AK} (mole dynamics)	g^0_{AK} (MDA)
1.03	1.90	1.85
1.08	2.53	2.55
1.13	2.40	2.51
1.19	1.90	1.96
1.23	1.55	1.64
1.26	1.35	1.43
1.31	1.15	1.16
1.35	0.96	1.01
1.38	0.85	0.92
1.46	0.75	0.75
1.51	0.67	0.70
1.54	0.65	0.69
1.56	0.65	0.69

The mean density approximation was applied to argon-krypton liquid mixtures at 116°K. Three mixtures with mole fraction of argon x_A being equal to 0.1, 0.5, and 0.9 were investigated. For each mixture, Mo, Gubbins, Jaccuci, and McDonald (1974) have reported g_{AA}, g_{AK}, and g_{KK}.

The radial distribution functions of the pure fluids were obtained by Verlet (1968) from equilibrium correlation functions for a dense classical fluid. These were interpolated to the desired values of r/σ, ϵ/kT, and $\rho(\bar{\sigma})^3$ in accordance with Equation (2). Interpolations with respect to r/σ and $\rho(\bar{\sigma})^3$ were done linearly, as the range of interpolation for these two parameters was quite small. Since the relation $g \cong \exp(-u/kT)$ is valid at low density, a linear interpolation of $\ln(g)$ with respect to $(1/T)$ was done to arrive at the desired value of ϵ/kT. The mean density approximation is effective in giving very good prediction of the separation distance at which the first peak occurs in the distribution function in the mixture. Results are shown in Tables 1, 2, and 3 and in comparison with the distribution function approximation of the original regular solution theory in Figure 1. The average error in the pair distribution function represented by Equation (2) was 4.1%.

THE MODIFIED REGULAR SOLUTION THEORY

The mean density approximation was applied in modifying the original regular solution theory developed by Hildebrand and Scott (1950). The following assumptions were made in the original theory:

1. The volume change on mixing is quite small, thus permitting us to write

$$\Delta A_v^e \cong \Delta G_p^e \tag{5}$$

2. The excess entropy per mole of mixture is given by

$$\Delta S^e = -R[x_1 \ln(\phi_1/x_1) + x_2 \ln(\phi_2/x_2)] \tag{6}$$

for molecules appreciably different in size. For similar size molecules Equation (6) approaches a value of zero for ΔS^e.

It can be shown (Hildebrand and Scott, 1950) that the molar configurational internal energy of a binary mixture considering only pair interactions is given by

$$E_M = 2\pi\rho_M N^2 \left[x_1^2 \int_0^\infty u_{11} g^M{}_{11} r^2 dr + 2x_1x_2 \int_0^\infty u_{12} g^M{}_{12} r^2 dr + x_2^2 \int_0^\infty u_{22} g^M{}_{22} r^2 dr \right] \tag{7}$$

where ρ_M is defined by $1/\rho_M = V_M = x_1V_1 + x_2V_2$, and V_1 and V_2 are the molar volumes of pure components 1 and 2, respectively. The molar configurational energy E_1 of pure 1 is

$$E_1 = 2\pi\rho_1 N^2 \int_0^\infty u_{11} g^0{}_{11} r^2 dr \tag{8}$$

From the definition of excess functions

$$\Delta E_v^e = E_M - x_1E_1 - x_2E_2 \tag{9}$$

The integral in Equation (8) represents the molar internal energy of 1 mole of component 1 less that of 1 mole of ideal gas at the same temperature and pressure. In other words, E_1 may be expressed as

$$E_1 = 2\pi\rho_1 N^2 \int_0^\infty u_{11} g^0{}_{11} r^2 dr = -(U_1^* - U_1) \tag{10}$$

The molar residual energy $(U^* - U)$ can also be calculated from an equation of state. If a Van der Waals equation of state is used, with V being the molar volume, then it can be shown that the constant a in the attraction term is

$$a = V(U^* - U) \tag{11}$$

At low pressures, $(U^* - U)$ for liquids is approximately equal to the energy of vaporization and may be expressed in terms of the solubility parameter δ which is defined by

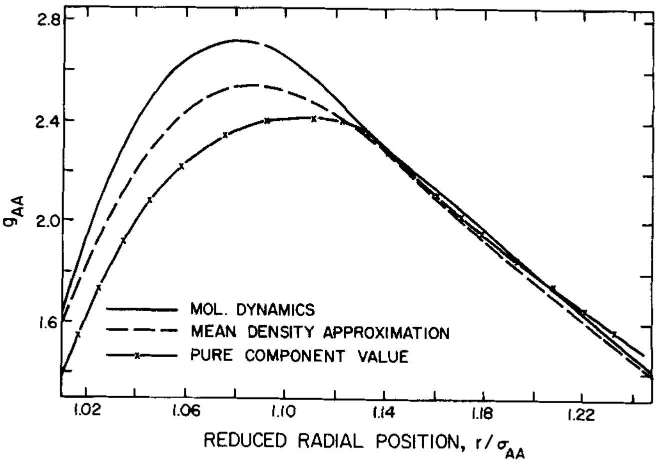

Fig. 1. Comparison of g_{AA} using mean density approximation and pure component values with mole dynamic results of Mo et al. (1974).

$$\delta = [(U^* - U)/V]^{0.5} \tag{12}$$

3. The original theory assumes that the integrals for each molecular pair, like Equation (10) for the 1-1 pairs, can be evaluated from pure component data expressed as solubility parameters and used to compute the integrals in Equation (7) for mixtures.

The modified theory retains the first two assumptions and attempts to improve on the third assumption by distinguishing between $g^0{}_{11}$ for pure components and $g^M{}_{11}$ for the 1-1 pair in the mixture. This is done by writing Equation (9) as

$$\Delta E_v^e = E_1 + E_2 + E_3 + E_4 + E_5 \tag{13}$$

where

$$E_1 = 2\pi\rho_M N^2 x_1^2 \int_0^\infty u_{11} g^M{}_{11} r^2 dr \tag{14}$$

$$E_2 = 2\pi\rho_M N^2 x_1 x_2 \int_0^\infty u_{12} g^M{}_{12} r^2 dr \tag{15}$$

$$E_3 = 2\pi\rho_M N^2 x_2^2 \int_0^\infty u_{22} g^M{}_{22} r^2 dr \tag{16}$$

$$E_4 = -2\pi\rho_M N^2 x_1 \int_0^\infty u_{11} g^0{}_{11} r^2 dr \tag{17}$$

and

$$E_5 = -2\pi\rho_M N^2 x_2 \int_0^\infty u_{22} g^0{}_{22} r^2 dr \tag{18}$$

Let

$$\rho_1' = \frac{(\bar{\sigma})^3 \rho_M}{\sigma^3{}_{11}} = \frac{1}{V_1'} \tag{19}$$

Then, from the mean density approximation

$$g^M{}_{11}(r, T, x_1, \rho_M) \cong g^0{}_{11}(r, T, \rho_1') \tag{20}$$

Similarly

$$g^M{}_{22}(r, T, x_1, \rho_M) \cong g^0{}_{22}(r, T, \rho_2') \tag{21}$$

where

$$\rho_2' = (\bar{\sigma})^3 \rho_M/\sigma^3{}_{22} \tag{22}$$

We now evaluate the expression on the right-hand side of Equation (13) term by term. It follows from Equations (10) and (20) that

$$E_1 = \frac{\rho_M}{\rho_1'} x_1^2 2\pi\rho_1' N^2 \int_0^\infty u_{11} g_{11}(r, T, \rho_1') r^2 dr = -x_1^2 \frac{\rho_M}{\rho_1'}(U_1^* - U_1') \tag{23}$$

TABLE 4. COMPARISON OF UNLIKE PAIR INTERACTION TERMS f_{12} AND m_{12} USED IN EQUATIONS (31) AND (32), RESPECTIVELY

System	Temperature (°C)	$1\text{-}m_{12}$	f_{12}
Benzene-pentane	25	1.006	1.015
Benzene-cyclopentane	25	0.982	0.990
Benzene-hexane	25	1.003	0.999
Benzene-2,methyl pentane	25	1.006	1.012
Benzene-2,2 dimethyl butane	25	1.015	1.020
Benzene-cyclohexane	25	0.985	0.995
Benzene-heptane	25	1.000	0.995
Benzene-2,4 dimethyl pentane	25	1.004	0.990
Benzene-2,2,3 trimethyl butane	25	1.014	1.022
Benzene-octane	25	1.003	0.989
Neopentane-cyclohexane	0	1.016	1.025
Cyclohexane-orthoxylene	50	0.990	0.988
Cyclohexane-orthoxylene	30	0.985	0.990
Cyclohexane-paraxylene	50	0.996	1.014

TABLE 5. COMPARISON OF UNLIKE PAIR INTERACTION TERMS f_{12} AND m_{12} WITH k_{12} VALUES OBTAINED BY STARLING AND HAN (1972)

System	T(°K)	$1\text{-}m_{12}$	f_{12}	$1\text{-}k_{12}$
Methane-propane	100	0.989	0.981	0.977
Methane-ethane	115.77	0.996	0.989	0.990

TABLE 6. SOURCES OF PURE COMPONENT DATA USED IN EQUATION (31) FOR THE MODIFIED REGULAR SOLUTION THEORY

Component	Molar volume	Internal energy/solubility parameter
Hexane	A	A
Cyclohexane	A	A
2-2 dimethyl butane	A	A
2 methyl pentane	A	A
Cyclopentane	A	A
2-4 dimethyl pentane	A	A
2-2-3 trimethyl butane	A	A
Heptane	A	A
Pentane	A	A
Octane	A	A
Methane	B	B
Ethane	B	B
Propane	B	B
Benzene	B	B
Orthoxylene	B	B
Paraxylene	B	B
Metaxylene	B	B
Neopentane	C	C

A—Funk and Prausnitz (1970).
B—Technical Data Book—Petroleum Refining, Vols. 1 and 2, American Petroleum Institute (1966).
C—Lyckman, Eckert, and Prausnitz (1965).

Making a Taylor series expansion about $V = V_1$ yields

$$E_1 = -x_1^2 \frac{\rho_M}{\rho_1'} \left\{ (U_1^* - U_1) + \left[\frac{\partial}{\partial V}(U_1^* - U_1) \right]_T (V_1' - V_1) \right\} \qquad (24)$$

From (11), $U^* - U = a(T)/V$. Therefore

$$\left[\frac{\partial}{\partial V}(U^* - U) \right]_T = -\delta^2 \qquad (25)$$

In Equation (23) $U_1^* - U_1'$ is evaluated at V_1' and T, whereas in Equation (24) $U_1^* - U_1$ is evaluated at V_1 and T. Using Equation (25), we get

$$E_1 = -x_1^2 \frac{\rho_M}{\rho_1'} \delta_1^2 (2V_1 - V_1') \qquad (26)$$

In similar fashion

$$E_3 = -x_2^2 \frac{\rho_M}{\rho_1'} \delta_2^2 (2V_2 - V_2') \qquad (27)$$

$$E_4 = x_1 \, \delta_1^2 \, V_1 \qquad (28)$$

and

$$E_5 = x_2 \, \delta_2^2 \, V_2 \qquad (29)$$

We assume that the unlike pair interaction can be represented by a mean geometric term; that is

$$E_2 = -2f_{12}(E_1 E_3)^{0.5} \qquad (30)$$

where f_{12} is the unlike pair interaction parameter which must usually be determined from experimental data. Using the assumption of constant volume, we may write

$$\Delta G_p^e \cong \Delta A_v^e \cong \Delta E_v^e - T\Delta S^e$$

The final result is

$$\Delta G_p^e = -x_1^2\delta_1^2(2V_1 - V_1')\left(\frac{\rho_M}{\rho_1'}\right) - x_2^2\delta_2^2(2V_2 - V_2')\left(\frac{\rho_M}{\rho_2'}\right) - 2f_{12}x_1x_2\delta_1\delta_2(2V_1 - V_1')^{0.5}(2V_2 - V_2')^{0.5}\left(\frac{\rho_M^2}{\rho_1'\rho_2'}\right)^{0.5} + RT\,[x_1 \ln(\phi_1/x_1) + x_2 \ln(\phi_2/x_2)] \qquad (31)$$

Equation (31) is defined as the modified regular solution theory (MRST). The corresponding equation from the regular solution theory is

$$\Delta G_p^e = (x_1V_1 + x_2V_2)\phi_1\phi_2[(\delta_1 - \delta_2)^2 + 2m_{12}\delta_1\delta_2] \qquad (32)$$

where m_{12} is the unlike pair interaction term introduced by Funk and Prausnitz (1970).

To remove uncertainties in the unlike pair interaction term in comparing the two theories, the pair coefficients f_{12} and m_{12} were obtained by fitting with the experimental data for each mixture at a point representing roughly equimolar composition. The two theories were then compared as to their ability to predict other compositions. The values of f_{12} and m_{12} obtained in this manner for different mixtures have been compiled in Table 4. The term k_{12} defined by $k_{12} = 1 - Tc_{12}/(Tc_1Tc_2)^{0.5}$ is a good approximation for the quantity $(1 - f_{12})$. The value of k_{12} can be determined from second virial cross coefficients (Prausnitz and Gunn, 1958) and is in good agreement with $(1 - f_{12})$ as shown in Table 5.

Table 6 lists the sources for the molar volumes and the solubility parameters of the pure components. The parameter σ_{ii} was, in accordance with the corresponding states principle, taken to be proportional to the cube root of the critical volume of component i. The constant of proportionality need not be known, since the σ_{ii} values appear as ratios of one to another.

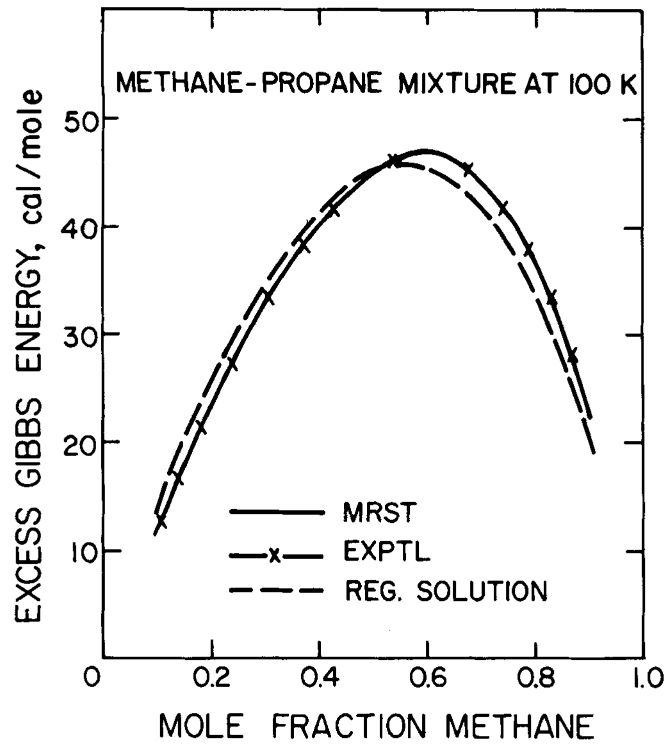

Fig. 2. Comparison of MRST with regular solution theory for predicting ΔG_p^e. Experimental values were taken from Cutler and Morrison (1965). Unlike pair coefficients obtained by fitting at 0.5 m.f. methane.

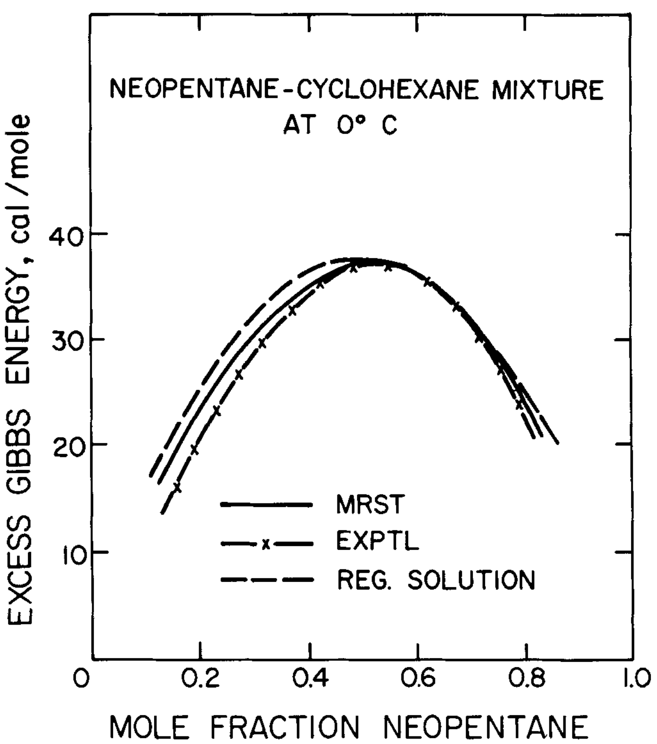

Fig. 3. Comparison of MRST with regular solution theory for predicting ΔG_p^e. Experimental values were taken from Mathot and Desmyter (1953). Unlike pair coefficients obtained by fitting at 0.55 m.f. neopentane.

RESULTS AND DISCUSSION

The modified regular solution theory was applied to nine binary mixtures of benzene with paraffins and cycloparaffins which were hexane, cyclohexane, 2-2 dimethyl butane, 2 methyl pentane, cyclopentane, 2-4 dimethyl pentane, 2-2-3 trimethyl butane heptane, and pentane. For these nine mixtures, the results of the MRST Equation (31) were in excellent agreement with the experimental data of Funk and Prausnitz (1970) who presented their results in the form of a Redlich-Kister correlation using fitted parameters which predicted the experimental ΔG_p^e with an average error of about 3%. However, it was observed that the original regular solution theory gave essentially the same results as the MRST. This was because the critical volumes of the two components in all these systems and therefore the molecular diameters were not greatly different. If $\sigma_{11} = \sigma_{22} = \sigma$ in Equation (19), then

$$\frac{V_1'}{V_M} = \frac{\sigma^3}{\sigma^3(x_1^2 + 2x_1x_2 + x_2^2)} = 1 = \frac{V_2'}{V_M}$$

and the MRST then collapses to the original regular solution theory. Hence the following systems with larger differences in their critical volumes were used to compare the results of Equation (31) with Equation (32): methane-propane at 100°K, neopentane-cyclohexane at 273°K, cyclohexane-orthoxylene at 323°K, orthoxylene-cyclohexane at 303°K, paraxylene-cyclohexane at 323°K, methane-ethane at 115.77°K, and benzene-octane at 298.15°K. The results are illustrated in Figures 2 to 8. The use of Equation (31) instead of Equation (32) results in an improve-

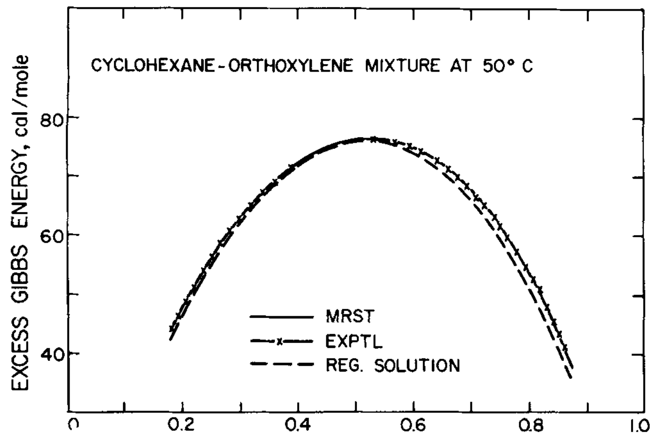

Fig. 4. Comparison of MRST and regular solution theory for predicting ΔG_p^e. Experimental values were taken from Jain and Yadav (1973). Unlike pair coefficients obtained by fitting at 0.47 m.f. cyclohexane.

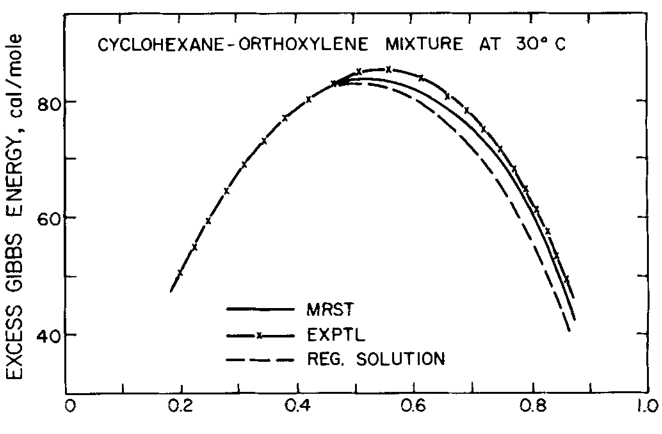

Fig. 5. Comparison of MRST with regular solution theory for predicting ΔG_p^e. Experimental values were taken from Jain and Yadav (1973). Unlike pair coefficients obtained by fitting at 0.41 m.f. cyclohexane.

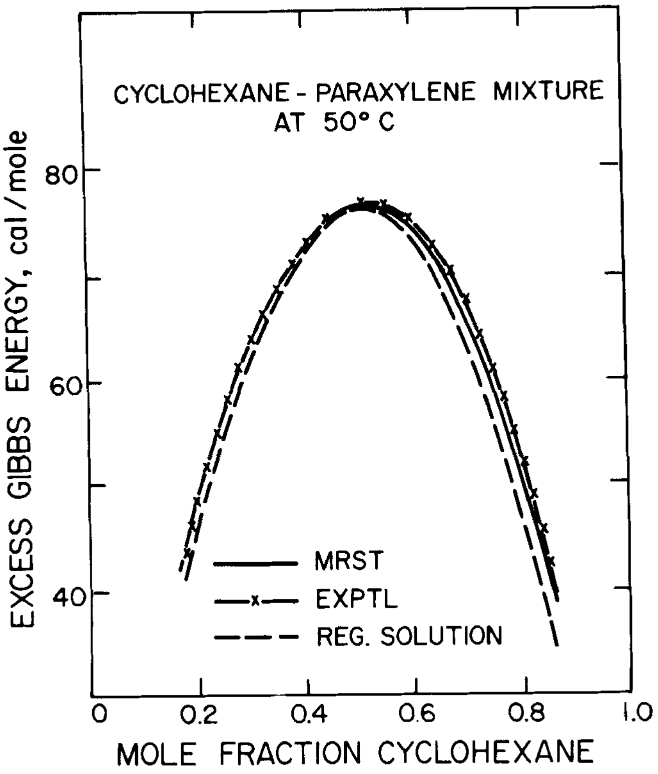

Fig. 6. Comparison of MRST with regular solution theory for predicting ΔG_p^e. Experimental values were taken from Jain and Yadev (1973). Unlike pair coefficients obtained by fitting at 0.45 m.f. cyclohexane.

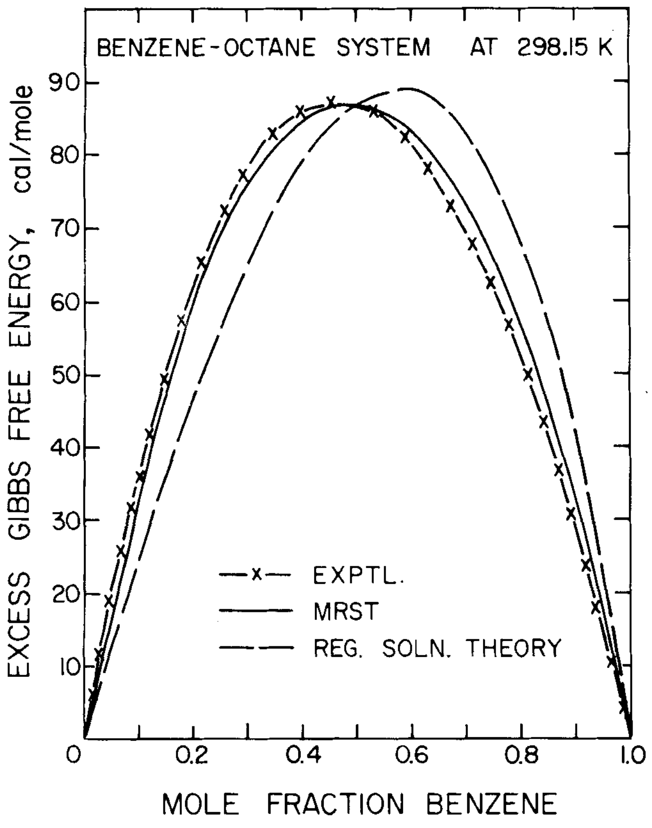

Fig. 8. Comparison of MRST with regular solution theory for predicting ΔG_p^e. Experimental values were taken from Funk and Prausnitz (1970). Unlike pair coefficients obtained by fitting at 0.5 m.f. benzene.

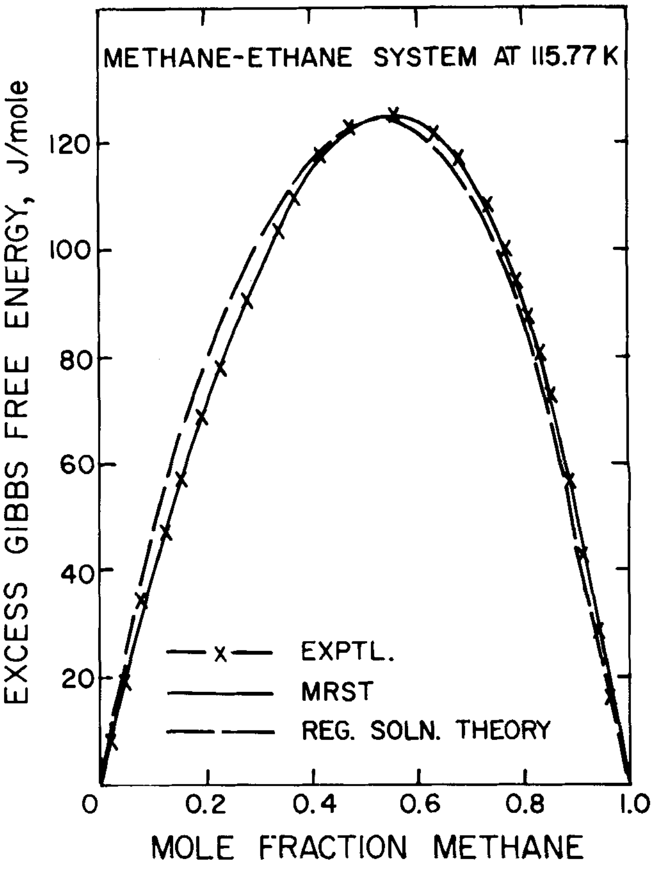

Fig. 7. Comparison of MRST with regular solution theory for predicting ΔG_p^e. Experimental values were taken from Miller and Staveley (1975). Unlike pair coefficients obtained by fitting at 0.5 m.f. methane.

ment of 7% in the prediction of ΔG_p^e for these mixtures.

The activity coefficient γ is obtained from

$$\gamma_1 = \exp\left(\frac{\Delta G_p^e + x_2\, \partial \Delta G_p^e/\partial x_1}{RT}\right) \tag{33}$$

$$\gamma_2 = \exp\left(\frac{\Delta G_p^e + x_1\, \partial \Delta G_p^e/\partial x_2}{RT}\right) \tag{34}$$

For systems at low pressures, the vapor phase can be considered to be ideal, in which case the following relation holds:

$$P = P_1^0 x_1 \gamma_1 + P_2^0 x_2 \gamma_2 \tag{35}$$

Table 7. Activity Coefficient and Vapor Pressure for Cyclohexane (1) + Orthoxylene (2) Mixture at 323.15°K

	Activity coeff., γ_1			Total pressure (torr)		
x_1	Exptl.	MRST	Reg. soln. theory	Exptl.	MRST	Reg. soln. theory
0.1788	1.363	1.321	1.301	86.43	87.52	80.25
0.3466	1.233	1.234	1.206	135.23	134.23	131.12
0.4374	1.177	1.170	1.152	156.46	156.41	153.45
0.5709	1.110	1.106	1.090	186.42	185.48	182.77
0.6565	1.074	1.072	1.085	204.30	203.50	208.85
0.7133	1.053	1.053	1.062	215.81	216.81	219.52
0.7807	1.033	1.033	1.039	229.69	228.08	233.85
0.8337	1.022	1.021	1.029	237.75	237.38	241.23
0.8722	1.012	1.015	1.016	248.20	247.26	252.56

Experimental values were taken from Jain and Yadav (1973).

Table 8. Excess Molar Enthalpy for Methane-Ethane System at 91.5°K

Mole fraction, methane	ΔH^e (exptl.), cal/mole	ΔH^e (MRST) cal/mole	ΔH^e (reg. soln.), cal/mole
0.1	6.3689	6.4752	6.9123
0.2	11.8086	11.9037	12.8925
0.3	16.1386	16.1762	16.6211
0.4	19.1713	19.1667	19.7775
0.5	20.7297	20.7301	20.7355
0.6	20.6297	20.6956	20.1524
0.7	18.6890	18.8656	18.0064
0.8	14.7254	15.0041	14.1358
0.9	8.5565	9.8293	8.1658

Experimental values were taken from Miller and Staveley (1975).

Calculations for the orthoxylene-cyclohexane system gave results in good agreement with experimental data and are listed in Table 7.

The excess molar enthalpy is computed from the equation

$$\frac{\partial}{\partial T}(\Delta G_p{}^e/T)_P = -\frac{\Delta H^e}{T^2} \qquad (36)$$

Calculations again showed good agreement with experiment for the methane-ethane system. These are appended in Table 8.

In conclusion, one may say that the mean density approximation is an improvement in the theory of structure of binary mixtures and removes one of the more serious assumptions of the older regular solution theory. The results indicate that a general theory of this type definitely benefits from an improved description of the structure of the fluid. A more correct expression for the structure needs to be considered along with corrections for volume and entropy changes on mixing.

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NOTATION

$\Delta A_v{}^e$ = excess Helmholtz energy per mole at constant volume
$\Delta E_v{}^e$ = excess internal energy per mole at constant volume
f_{12} = unlike pair interaction term used in Equation (31)
g = radial distribution function
$\Delta G_p{}^e$ = excess Gibbs energy per mole at constant pressure
k = Boltzmann's constant
ΔH^e = excess enthalpy per mole
m_{12} = unlike pair interaction term used in Equation (32)
N = Avogadro's number
P = pressure
r = radial coordinate
R = universal gas constant
ΔS^e = excess entropy per mole
T = temperature
Tc = critical temperature
u = intermolecular potential
U = internal energy per mole
V = volume per mole
x = mole fraction

Greek Letters

δ = solubility parameter
ϵ = force parameter in the intermolecular potential model
γ = activity coefficient
ϕ = volume fraction, $= V/V_M$
ρ = molar density, $= 1/V$
σ = size parameter in the intermolecular potential model
λ = correction factor for σ_{12}

Superscripts

e = excess quantity
M = mixture
0 = pure component
$*$ = ideal state

Subscripts

1, 2 = components 1 and 2, respectively
p, v = constant pressure and volume, respectively
M = mixture

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