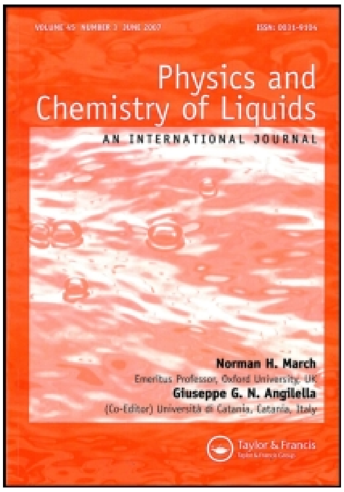

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Activity coefficients of non-electrolyte liquid binary systems under pressure

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Activity Coefficients of Non-Electrolyte Liquid Binary Systems under Pressure

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The pressure dependence of the activity coefficients in seven binary non-electrolyte mixtures is calculated. Experimental PVT data for pure components and mixtures are interpolated to give the molar volumes at specific pressures. The partial molar volume along isobars is calculated as a function of composition and the excess partial molar volume is integrated numerically along constant composition lines. The adequacy of the calculations is discussed. The results obtained on all systems are physically reasonable and consistent with thermodynamic data at 1 atm., and the Gibbs-Duhem equation has been used to show that they are mathematically (as distinct from thermodynamically) consistent. The effect of pressure is found to vary: systems may become more or less ideal or the activity coefficients may be unaltered with increasing pressure. Possible sources of the difference in the pressure dependence of the systems are discussed briefly.

1. INTRODUCTION

As part of a continuing study of transport processes in liquids, we have constructed apparatus for diffusion measurements at pressures up to 2000 atm.[1]

The conventional theoretical analysis of mutual diffusion data requires activity coefficient derivatives.[2] However, a thorough literature survey has yielded no specific calculation of activity coefficients in non-electrolyte liquid systems at elevated pressures. Since numerous chemical processes are carried out at high pressures and high pressure fluid behavior is of great importance in the petroleum industry,[3] the absence of activity data for liquid systems at high pressures is surprising. Liquid-phase activity coefficients are usually assumed to be unaffected by pressure provided it remains moderate, but such an assumption could lead to serious error at high pressures.[4] Conventional techniques for measuring activity coefficients in non-electrolyte systems become almost prohibitively difficult at high pressures. However, PVT data for liquid mixtures can provide a source of activity coefficients. In this paper, we show how such data can be employed and discuss some numerical schemes for calculating the effect of pressure on the activity of binaries. Finally, we present calculations on seven non-electrolyte liquid mixtures at 25°C for which adequate PVT data exist.

Our primary concern in this paper is to ascertain (i) if reliable estimates of the pressure dependence of activity coefficients in these liquid mixtures can be obtained from PVT data; and (ii) the qualitative and quantitative changes in the activity coefficients with pressure. Being primarily concerned with the method, we have avoided mixtures involving water or alcohols where changes might be deceptively large, and n-alkane mixtures with similar carbon numbers where the changes might be unrepresentatively small.

2. THEORY

The information we review in this section is available in most texts on thermodynamics; the following approach and nomenclature is that of Prausnitz.[3] The activity coefficient of component i in a liquid mixture is related to the fugacity f_i^L by

$$f_i^L = \gamma_i x_i f_i^o \tag{1}$$

where γ_i is the activity coefficient , x_i is the mole fraction of i in the mixture, and f_i^o is the fugacity of i at the standard state.

Since we are dealing with the liquid phase and large pressure changes in this work, the standard state is defined as that of the pure component at the *same temperature and pressure* as the mixture.[3]

Taking the logarithm of Eq. (1) and differentiating with respect to pressure at constant temperature and composition, we obtain

$$\left(\frac{\partial \ln f_i^L}{\partial P}\right)_{T,x} = \left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} + \left(\frac{\partial \ln f_i^o}{\partial P}\right)_{T,x} \tag{2}$$

Using the thermodynamic relations

$$\left(\frac{\partial \ln f_i}{\partial P}\right)_{T,x} = \frac{\hat{v}_i}{RT}; \quad \left(\frac{\partial \ln f_i^o}{\partial P}\right)_{T,x} = \frac{v_i}{RT} \tag{3}$$

where $\hat{v}_i$ is the partial molar volume of component i in the liquid mixture and v_i is the molar volume of pure i, Eq. (2) can be expressed as

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{\hat{v}_i - v_i}{RT} \tag{4}$$

It then follows that

$$\ln\left(\frac{\gamma_i^P}{\gamma_i^1}\right) = \int_{P=1}^{P} \left(\frac{\hat{v}_i - v_i}{RT}\right) dP \tag{5}$$

Clearly Eq. (5) expresses the effect of pressure on the activity coefficient of i in terms of PVT properties at constant composition. However, partial molar volumes are not measured directly, but in binary systems can be obtained from

$$\hat{v}_1 = v - x_2 \left(\frac{\partial v}{\partial x_2}\right)_{T,P} \tag{6}$$

where v is the volume of one mole of a 1,2 mixture. This implies that sufficient composition data must be available for a reasonable value of $\left(\frac{\partial v}{\partial x_2}\right)_{T,P}$ to be obtained.

3. NUMERICAL SCHEMES

Frequently, PVT data for liquids are fitted to a Huddleston equation:[5]

$$v_P = v_O (1 + A_1 P + A_2 P^2 + A_3 P^3 ---) \tag{7}$$

or a Tait equation[6]

$$v_P = v_O (1 - C \log [1 - B/P]) \tag{8}$$

Fitting v_1, the molar volume of the mixture of 1 atm., as a function of the composition, in theory, one can obtain an analytic expression for the excess volume ($\hat{v} - v_i$) as a function of pressure and composition, and therefore for the effect of pressure on the activity coefficient. Alternatively, one can take volume-composition data along various isobars and compile excess volumes on a grid of pressure and composition. Numerical integration along a constant composition line with respect to pressure can then be performed.

If the self-consistency of the PVT data is sufficiently good and a sufficient number of coefficients in the pressure and composition series are used, the two techniques should be identical. Agreement between the methods suggests that a reasonable, but not necessarily correct, assessment of the effect of pressure on the activity coefficients has been obtained. Similarly, the Gibbs-Duhem equation

$$\partial \ln \left(\frac{\gamma_1^P}{\gamma_1^1}\right) = -\frac{x_2}{x_1}\,\partial \ln \left(\frac{\gamma^P{}_2}{\gamma^1{}_2}\right) \qquad (9)$$

provides a check of mathematical, but not thermodynamic, consistency since the use of Eq. (6) involves the equality expressed in Eq. (9). The activity coefficient ratio, or ACR $(\gamma^P/\gamma^1)_2$, can be calculated directly from the PVT data or from the ratio $(\gamma^P/\gamma^1)_1$ using Eq. (9). The two values should of course be identical.

4. EXPERIMENTAL PVT DATA

Since it was decided not to consider alkane mixtures where only small deviations from ideal behavior might be expected, or water or alcohol mixtures where the changes in non-ideality could conceivably be very large, only three sets of data were found which could be studied. These were:

i) benzene-cyclohexane and benzene-carbon tetrachloride data in the form of Eq. (7) applicable to a maximum of 400 atm. for the pure components and three mixtures;[5]

ii) aniline-benzene, aniline-chlorobenzene and aniline-nitrobenzene data in the form of Eq. (8) up to 1500 atm. for the pure components and three compositions,[6] and aniline-nitrobenzene for an additional six mixtures;[7] and

iii) isothermal compressibility data to 600 atm. for the pure components and nine mixtures of benzene-carbon tetrachloride, benzene-ethylene dichloride and chloroform-diethyl ether.[8]

(i) and (ii) can be treated either analytically or numerically as discussed in the previous section, but for (iii) a somewhat different approach is necessary. In view of the limited amount of available data and the fact that experimental results were reported by Dolezalek and Speidel for a large number of compositions,[8] the conversion of their data for isothermal compressibilities to a form suitable for the present analysis was considered worthwhile.

The isothermal compressibility is defined by

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad (10)$$

If the molar volume of a liquid can be expressed by Eq. (7), then we can write

$$\beta_T = -\frac{A_1 + 2A_2P + 3A_3P^2}{1 + (A_1P + A_2P^2 + A_3P^3)} \qquad (11)$$

The denominator in Eq. (11) can be expanded in a binomial series of $(A_1P + A_2P^2 + A_3P^3)$:

$$\begin{aligned} \beta_T = -&[A_1 + 2A_2P + 3A_3P^2] \\ &[1 - (A_1P + A_2P^2 + A_3P^3) \\ &+ (A_1P + A_2P^2 + A_3P^3)^2 \\ &+ (A_1P + A_2P^2 + A_3P^3)^3 ----] \end{aligned} \qquad (12)$$

Simplifying Eq. (12) and collecting terms in P, we write

$$\beta_T = - A_1 + (A_1^2 - 2A_2)\,P + (3A_1A_2 - A_1^3 - 3A_3)\,P^2 ---- \qquad (13)$$

Therefore, by fitting the β_T data of Dolezalek and Speidel[8] (which form smooth curves when plotted against composition) in a series in P

$$\beta_T = E_0 + E_1P + E_2P^2 ---- \qquad (14)$$

the coefficients A_i in Eq. (11) can be identified:

$$\begin{aligned} A_1 &= - E_0 \\ A_2 &= 1/2\,(A_1^2 - E_1) \\ A_3 &= A_1A_2 - 1/3\,(E_2 + A_1^3) ---- \end{aligned} \qquad (15)$$

The replacement of Eq. (11) by Eq. (14) involves a negligible truncation error. Using the coefficients obtained by Eq. (15) for each composition, a P-V-x grid was constructed for the Dolezalek-Speidel data.[8] Similar grids were constructed from Eqs. (7) and (8) for the Holder-Whalley[5] and Gibson-Loeffles[6,7] data.

5. NUMERICAL CALCULATIONS

If the molar volume of a liquid mixture at 1 atm. is fitted by a series in the mole fraction of component j, the volume at pressure P can be written as

$$v_p = (D_0 + D_1x_j + D_2x_j^2 ---)\frac{(1 + A_1P + A_2P^2 + A_3P^3 ---)}{(1 + A_1 + A_2 + A_3)} \qquad (16)$$

where D_i are the coefficients of x_j at 1 atm. and A_i are also functions of x_j. The corresponding expression for the partial molar volume, Eq. (6), is consequently more complicated, but if the coefficients A_i are also fitted by expansion in x_j, the integration in Eq. (5) can be carried out analytically. This development is quite straightforward but lengthy, so that the expressions are not reported here. While reasonable agreement was obtained between the analytical method and the numerical solution discussed below, the latter approach is preferred because it is simpler and makes more direct use of the experimental data in those cases where they are reported.

In the numerical evaluation of Eq. (5), a series of molar volumes were calculated for a range of pressures at each experimental composition using Eq. (7) for the Holder-Whalley data,[5] Eq. (8) for the Gibson-Loeffler data[6,7] and the method previously described for the Dolezalek-Speidel data.[8] Along each isobar, the partial molar volume of each component and the excess molar volume $(\bar{v}_1 - v_1)$ were calculated from Eq. (6). This calculation was done in two ways. First, the molar volume for each isobar was fitted to an expansion in terms of composition, so that an analytic expression for $\bar{v}_1$ for all compositions was obtained. This is subsequently referred to as a PS (for power series) fit. The pressure dependence of the activity coefficient at mole fractions of 0.1 to 0.9 and 0.99 was then obtained using a Simpson's rule integration with a step length of 10 atm. between 1 and 100 and increments of 100 atm. thereafter. In the alternative approach, the molar volume at each isobar was fitted by a cubic SPLINE routine. Since the use of this routine required the slope, $\frac{\partial V}{\partial x_1}$, at $x_1 = 0$ and $x_1 = 1.0$, the first and last three composition points respectively were fitted by a parabola and the analytic expressions for the slopes were used as additional input data. This cubic spline technique is subsequently referred to as a CS fit. $(\bar{v}_1 - v_1)$ values were calculated at the required x_1 and the integrals were again evaluated by Simpson's rule.

To ensure that these calculations were carried out consistently, Eq. (9) was used to calculate the activity coefficient of each component of the binary. The function ${}^{x}/(1-x)$ was fitted as a function of the estimated $\ln(\gamma^P/\gamma^1)$ using a 4 point Lagrangian, and the integration was performed analytically in each segment and a cumulative sum performed.

6. RESULTS

ACR data are tabulated for both components in terms of the mole fraction of one component up to the maximum pressure for which Eqs. (7) and (8) produce well-behaved results. It should be noted that for the data of Holder and Whalley[5] and Dolezalek and Speidel,[8] this is in excess of the maximum experimental pressure by 200 atm. The results reported in Table 1 have been calculated according to the second scheme discussed in the previous section, i.e. volumes at each isobar were fitted by a three coefficient series in mole fraction, allowing the excess volume to be calculated for all desired compositions at each isobar and integration with respect to pressure being performed numerically along constant composition lines.

Results for five of the systems at specific pressures are plotted in the form ACR vs. x in Figures 1-3. The effect of pressure on the activity coefficients in the benzene-ethylene dichloride system shown in Figure 1 is representative of all the systems studied, though in the cases of aniline-benzene and chloroform-ether,

TABLE 1

The effect of pressure on the activity coefficients in binary mixtures at 25° C.

System	Pressure (atm)	Composition (x_1)					
		0.01	0.2	0.4	0.6	0.8	0.99
		(γ^P/γ^1) Component (1)					
Benzene (1) – carbon tetrachloride (2) [a]	50	1.0007	1.0004	1.0001	1.0000	1.0000	1.0000
	100	1.0012	1.0006	1.0002	1.0001	1.0000	1.0000
	200	1.0022	1.0012	1.0005	1.0002	1.0000	1.0000
	300	1.0023	1.0026	1.0021	1.0012	1.0004	1.0000
	400	1.0008	1.0034	1.0038	1.0024	1.0008	1.0000
		(γ^P/γ^1) Component (2)					
	50	1.0000	1.0000	1.0001	1.0002	1.0003	1.0003
	100	1.0000	1.0001	1.0002	1.0004	1.0005	1.0005
	200	1.0000	1.0001	1.0004	1.0008	1.0010	1.0012
	300	1.0000	1.0000	1.0003	1.0012	1.0032	1.0065
	400	1.0000	1.0000	1.0000	1.0011	1.0049	1.0119

[a] Based on the data of Holder and Whalley[5]

		(γ^P/γ^1) Component (1)					
Benzene (1) – cyclohexane (2)	50	1.0064	1.0041	1.0022	1.0010	1.0002	1.0000
	100	1.0111	1.0071	1.0039	1.0017	1.0004	1.0000
	200	1.0206	1.0133	1.0074	1.0032	1.0008	1.0000
	300	1.0387	1.0257	1.0148	1.0067	1.0017	1.0000
	400	1.0442	1.0298	1.0174	1.0080	1.0021	1.0000
		(γ^P/γ^1) Component (2)					
	50	1.0000	1.0003	1.0011	1.0023	1.0040	1.0060
	100	1.0000	1.0005	1.0018	1.0040	1.0070	1.0106
	200	1.0000	1.0009	1.0034	1.0075	1.0132	1.0200
	300	1.0000	1.0015	1.0062	1.0142	1.0261	1.0411
	400	1.0000	1.0017	1.0070	1.0164	1.0305	1.0488

		$(\gamma P/\gamma 1)$ Component (1)					
Aniline (1) – benzene (2)	200	0.9907	0.9941	0.9968	0.9986	0.9997	1.0000
	400	0.9812	0.9876	0.9929	0.9968	0.9992	1.0000
	600	0.9803	0.9853	0.9906	0.9954	0.9987	1.0000
	800	0.9851	0.9855	0.9889	0.9938	0.9981	1.0000
	1000	0.9941	0.9876	0.9880	0.9924	0.9975	1.0000
	1200	1.0032	0.9905	0.9878	0.9915	0.9971	1.0000
	1400	1.0063	0.9923	0.9887	0.9919	0.9972	1.0000
		$(\gamma P/\gamma 1)$ Component (1)					
	200	1.0000	0.9996	0.9985	0.9966	0.9941	0.9912
	400	1.0000	0.9993	0.9970	0.9931	0.9875	0.9807
	600	1.0000	0.9994	0.9971	0.9923	0.9843	0.9732
	800	1.0000	0.9999	0.9983	0.9933	0.9829	0.9665
	1000	1.0000	1.0007	1.0004	0.9956	0.9831	0.9612
	1200	1.0000	1.0014	1.0023	0.9982	0.9844	0.9587
	1400	1.0000	1.0015	1.0028	0.9993	0.9861	0.9608
		$(\gamma P/\gamma 1)$ Component (1)					
Aniline (1) – chlorobenzene (2)	200	1.0052	1.0027	1.0011	1.0003	1.0000	1.0000
	400	1.0141	1.0062	1.0017	1.0000	1.0000	1.0000
	600	1.0206	1.0093	1.0028	1.0001	0.9998	1.0000
	800	1.0267	1.0131	1.0049	1.0011	1.0000	1.0000
	1000	1.0317	1.0176	1.0081	1.0028	1.0005	1.0000
	1200	1.0361	1.0223	1.0119	1.0050	1.0012	1.0000
	1400	1.0405	1.0267	1.0152	1.0068	1.0017	1.0000
		$(\gamma P/\gamma 1)$ Component (2)					
	200	1.0000	1.0003	1.0010	1.0018	1.0024	1.0025
	400	1.0000	1.0009	1.0027	1.0044	1.0046	1.0025
	600	1.0000	1.0013	1.0040	1.0065	1.0071	1.0043
	800	1.0000	1.0015	1.0050	1.0087	1.0109	1.0101
	1000	1.0000	1.0016	1.0056	1.0108	1.0160	1.0197
	1200	1.0000	1.0016	1.0060	1.0129	1.0217	1.0315
	1400	1.0000	1.0016	1.0065	1.0149	1.0269	1.0419

		$(\gamma P/\gamma 1)$ Component (1)					
Aniline (1) – nitrobenzene (2)	200	1.0080	1.0062	1.0040	1.0020	1.0006	1.0000
	400	1.0181	1.0139	1.0090	1.0045	1.0013	1.0000
	600	1.0252	1.0193	1.0125	1.0063	1.0018	1.0000
	800	1.0319	1.0245	1.0159	1.0080	1.0022	1.0000
	1000	1.0385	1.0294	1.0191	1.0096	1.0027	1.0000
	1200	1.0448	1.0342	1.0222	1.0111	1.0031	1.0000
	1400	1.0509	1.0389	1.0251	1.0126	1.0035	1.0000
		$(\gamma P/\gamma 1)$ Component (2)					
	200	1.0000	1.0002	1.0012	1.0032	1.0066	1.0116
	400	1.0000	1.0005	1.0027	1.0072	1.0150	1.0261
	600	1.0000	1.0007	1.0037	1.0100	1.0208	1.0364
	800	1.0000	1.0009	1.0047	1.0127	1.0264	1.0462
	1000	1.0000	1.0011	1.0056	1.0152	1.0317	1.0557
	1200	1.0000	1.0013	1.0065	1.0177	1.0369	1.0649
	1400	1.0000	1.0015	1.0074	1.0201	1.0419	1.0738
		$(\gamma P/\gamma 1)$ Component (1)					
Benzene (1) – carbon tetrachloride (2)[b]	50	1.0007	1.0003	1.0001	1.0000	1.0000	1.0000
	100	1.0011	1.0005	1.0001	1.0000	1.0000	1.0000
	200	1.0020	1.0008	1.0002	1.0000	1.0000	1.0000
	400	1.0032	1.0010	0.9999	0.9997	0.9998	1.0000
	600	1.0048	1.0015	0.9999	0.9996	0.9998	1.0000
	800	1.0084	1.0034	1.0007	0.9998	0.9998	1.0000
		$(\gamma P/\gamma 1)$ Component (2)					
	50	1.0000	1.0000	1.0001	1.0002	1.0002	1.0002
	100	1.0000	1.0001	1.0002	1.0004	1.0004	1.0001
	200	1.0000	1.0001	1.0004	1.0006	1.0006	1.0001
	400	1.0000	1.0003	1.0007	1.0009	1.0004	0.9986
	600	1.0000	1.0004	1.0011	1.0014	1.0007	0.9983
	800	1.0000	1.0006	1.0018	1.0026	1.0022	0.9999

[b] Based on the data of Dolezalek and Speidel[8].

		$(\gamma P/\gamma 1)$ Component (1)					
Chloroform (1) – ether (2)	50	0.9866	0.9922	0.9961	0.9985	0.9997	1.0000
	100	0.9777	0.9870	0.9937	0.9976	0.9995	1.0000
	200	0.9600	0.9768	0.9887	0.9958	0.9991	1.0000
	400	0.9289	0.9593	0.9807	0.9931	0.9987	1.0000
	600	0.9072	0.9467	0.9747	0.9910	0.9983	1.0000
	800	0.8735	0.9267	0.9650	0.9875	0.9977	1.0000
		$(\gamma P/\gamma 1)$ Component (2)					
	50	1.0000	0.9994	0.9977	0.9953	0.9927	0.9902
	100	1.0000	0.9989	0.9961	0.9922	0.9879	0.9840
	200	1.0000	0.9980	0.9930	0.9860	0.9784	0.9716
	400	1.0000	0.9964	0.9872	0.9751	0.9626	0.9526
	600	1.0000	0.9952	0.9831	0.9672	0.9510	0.9382
	800	1.0000	0.9933	0.9766	0.9548	0.9326	0.9151
		$(\gamma P/\gamma 1)$ Component (1)					
Benzene (1) – ethylene dichloride (2)	50	1.0055	1.0041	1.0026	1.0013	1.0004	1.0000
	100	1.0098	1.0073	1.0046	1.0023	1.0006	1.0000
	200	1.0184	1.0137	1.0087	1.0043	1.0012	1.0000
	400	1.0428	1.0317	1.0201	1.0099	1.0027	1.0000
	600	1.0615	1.0454	1.0286	1.0140	1.0039	1.0000
	800	1.0806	1.0592	1.0371	1.0182	1.0050	1.0000
		$(\gamma P/\gamma 1)$ Component (2)					
	50	1.0000	1.0002	1.0008	1.0022	1.0044	1.0074
	100	1.0000	1.0003	1.0015	1.0038	1.0077	1.0132
	200	1.0000	1.0006	1.0028	1.0072	1.0145	1.0249
	400	1.0000	1.0013	1.0064	1.0166	1.0338	1.0582
	600	1.0000	1.0019	1.0091	1.0237	1.0483	1.0836
	800	1.0000	1.0025	1.0118	1.0309	1.0630	1.1093

Estimated melting curve[12,26] - - - - -

the ACR is less than unity and for benzene-carbon tetrachloride the ACR does not differ significantly from unity.

7. DISCUSSION

In the first part of this section, we will discuss the accuracy of the calculations, their limitations and the effectiveness of the various numerical schemes. In the latter part, we will consider the behavior of the ACR under pressure in the

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† In carrying out the calculations, we have treated the two sets of C_6H_6-CCl_4 data as independent systems.

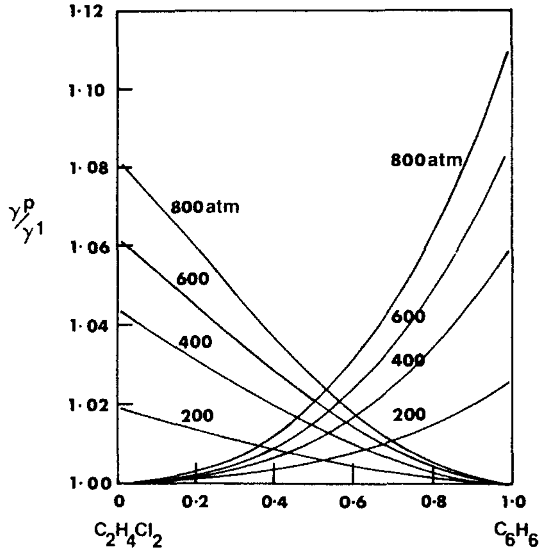

FIGURE 1 The effect of pressure on the activity coefficients in the system benzene-dichloroethane.

individual systems and discuss possible causes for the different behavior.

Of the eight systems considered,[†] PVT data were reported for four at only 5 compositions (3 mixtures and the two pure components).[5,6] Even where the V-x isobars are well-behaved, 5 compositions are barely adequate for the present calculations. Clearly the number of coefficients employed in the PS fit is limited, but even under these circumstances, the PS fit appears more reasonable than a CS fit which produces an ACR which oscillates about the PS fit as the composition varies. The latter becomes more successful when more composition data are available. In Figure 2, we see the two numerical schemes compared for aniline-benzene (5 compositions) at 600 atm. and aniline-nitrobenzene (8 compositions) at 800 atm. The results from the CS fit are seen to wave around the PS fit for aniline-benzene, but slightly better agreement is obtained for the aniline-nitrobenzene system. The difference between the PS and CS fits was in fact worse for the aniline-benzene system than for the other 4 systems. A PS fit to third order proved adequate for all systems probably because the excess volume was never large and was relatively symmetrical. It is conceivable that in systems where strong association is possible, a CS fit would be better; in such cases where extrema or inflection points in the V-x isobars are possible, a series expansion might produce a poor fit.

The overall agreement between CS and PS fits in the first five systems is encouraging. It can also be seen in Figure 3 that having calculated the ACR of

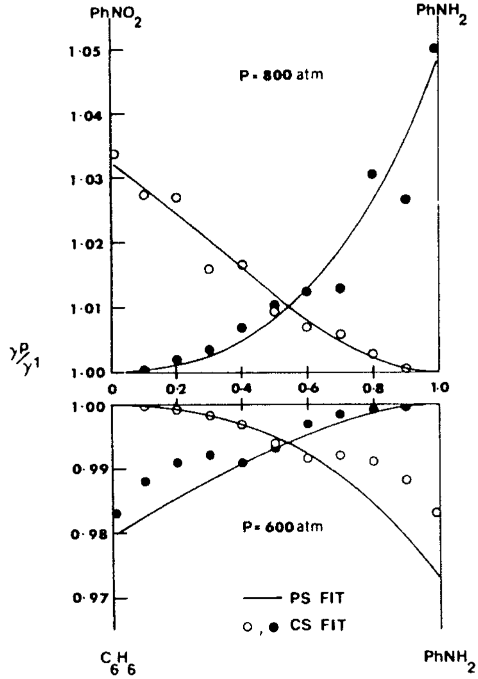

FIGURE 2 A comparison of the activity coefficient ratios calculated by power series (PS) and cubic spline (CS) fits of V-x isobars in the systems aniline-benzene at 600 atm. and aniline-nitrobenzene at 800 atm.
__________PS Fit; ●,o CS Fit

one component from the PVT data, the application of the Gibbs-Duhem equation produces good agreement with the direct calculation of the ACR of the second component.

We can compare the two sources of data for the system, C_6H_6-CCl_4, noting that comparatively different values of the isothermal compressibility of the pure components were found.[5,8] Calculations performed on both sets of data show that the ideality characteristic of this system at 1 atm persists at higher pressures also. It is necessary to carry a large number of figures to distinguish between the two sets of data. Noting that a larger uncertainty than this is associated with conventional activity coefficient measurements at 1 atm. and that some error must be introduced in converting β_T data to molar volumes, we consider the agreement is very good. We can infer that PVT measurements on binary liquids require selfconsistency rather than exceptional accuracy to provide a reasonable estimate of the effect of pressure on the activity coefficients.

A quick glance at Table 1 establishes that increasing the pressure on a binary liquid system may increase the activity coefficients (eg. C_6H_6-C_6H_{12}), decrease them (eg. $CHCl_3$-Et_2O), or have essentially no effect on them (eg. C_6H_6-CCl_4).

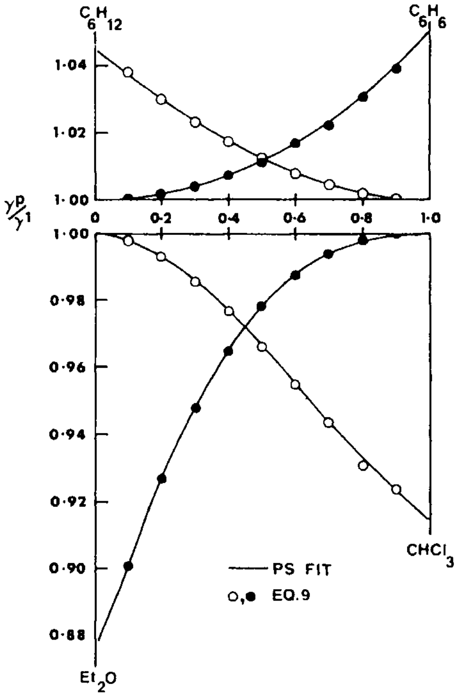

FIGURE 3 A comparison of the activity coefficient ratios calculated directly from a PS fit and from the Gibbs-Duhem equation in the systems benzene-cyclohexane at 400 atm. and chloroform-ether at 800 atm.

_________PS Fit; •,o Eq. (9)

While our consideration has been limited to only 7 systems, they cover a range in behavior, and have the additional advantage that we can examine the differences in four benzene and three aniline systems.

Benzene systems

CCl_4: As previously noted, this system is virtually unaffected by pressure. A 1% increase in the activity coefficient of CCl_4 at the highest pressure and benzene composition is indicated by the data of Holder and Whalley,[5] but this is possibly due to extrapolating their data beyond the experimental maximum of 250 atm. The less reliable data of Dolezalek and Speidel[8] show no significant change in activity up to 800 atm.

C_6H_{12} : the ACR's for this system at 400 atm. are shown in Figure 3 and indicate a 5% increase in limiting values of the activity coefficients of 1 atm. The symmetry is displaced slightly to the benzene-rich side ($x_B = 0.51$ is where the two curves intersect). This agrees well with the data of Donald and Ridgeway[9] at 1 atm. which show $\ln \gamma_B/\gamma_C = 0$ at $x_B = 0.51$ and with observations of the maximum in the excess heat in mixtures slightly rich in benzene.[10]

$C_2H_4Cl_2$: Figure 1 indicates $\left(\gamma^P/\gamma^1\right)_1 = \left(\gamma^P/\gamma^1\right)_2$ at $x_B = 0.54$ at all pressures at 25°C. Using density data at 20°C,[11] Rowlinson has calculated the quantity $\left[-x^2 \frac{\partial V}{\partial x}\right]$ for each component and shows them to be equal at $x_B = 0.53$.[10] This quantity is of course directly related to the activity coefficient. While this system obeys Raoult's law, it is not ideal by other definitions or observations; [10] although $C_2H_4Cl_2$ displays come polarity, this introduces no special effects in this system.[3]

$C_6H_5NH_2$: this proved to be the most difficult to fit with the present calculations, and as we have mentioned above and shown in Figure 2, the agreement between the PS and CS fits is only fair. Furthermore, it would seem to be fortuitous that a melting curve obtained by linear interpolation of the freezing pressures of the pure components at 25°C[12] separates the physically incorrect results from the PS fit. There is no reason why the Tait equation should not provide reasonable results when extrapolated beyond the experimental range. However, for all the pure components and mixtures they studied, Gibson and Loeffler set the constant C in Eq. (8) at 0.21591. We believe that the resultant loss of flexibility in the Tait equation probably leads to the unphysical behavior at higher pressures. This system has been thoroughly studied recently by Deshpande and Pandya[13] who found that the maximum in the excess free energy and $(\gamma_B/\gamma_A) = 1.00$ at $x_B = 0.57 \pm .01$ at 25, 35 and 45°C. Earlier work at higher temperatures found $\gamma_B = \gamma_A$ at $x_B = 0.50$ and G^E_{max} at $x_B = 0.47$[14], and again that the system was almost symmetrical in G^E with $\gamma_B = \gamma_A$ at $x_B = 0.525$.[15] These may be compared with the present result from a PS fit: $(\gamma^P/\gamma^1)_1 = (\gamma^P/\gamma^1)_2$ at $x_B = 0.54$.

Aniline systems

C_6H_6: we have discussed this system above, noting that the activity coefficients decrease with increasing pressure.

$C_6H_5NO_2$: as indicated in Table I and shown in Figure 2, the aniline-nitrobenzine system shows an increase in non-ideality with increasing pressure. $(\gamma^P/\gamma^1)_1 = (\gamma^P/\gamma^1)_2$ at $x_A = 0.54$ but no results are available in the literature for excess molar properties other than volume for this system. Predictions of the ACR based on Eq. (8) are well-behaved for this system well above the approximate melting curve in contrast to the results for aniline-benzene mixtures.

C_6H_5Cl: this system is similar in behavior to aniline-nitrobenzene but while non-ideality increases with increasing pressure, the effect is less marked. The present calculations indicate an almost perfectly symmetrical effect of pressure on the activity coefficients. Measurements at 1 atm and 25°C indicate that $\gamma_C = \gamma_A$ and a maximum in free energy occur at $x_A = 0.45$.[13]

Chloroform-ether

This is an example of a system which involves the specific interaction between the unlike molecules, such that 1-2 pairing dominates over 1-1 and 2-2 parings. The hydrogen atom of the chloroform molecule forms a hydrogen bond with the oxygen atom of the ether molecule.[10] At 1 atm., negative deviations from ideality–activity coefficients less than unity–result from the solvation of chloroform and ether.[17] The increase in pressure favors complex formation and results in decreases in the activity coefficients (see Figure 3). Activity coefficients calculated from surface tension measurements in this system at 33°C yielded $(\gamma_C/\gamma_E) = 1.00$ at $x_c = 0.54$[18] and recent measurements of the heat mixing indicate that the maximum occurs at $x_c = 0.53$.[19] These results are in reasonable agreement with the present calculations which show $(\gamma^p/\gamma^1)_C = (\gamma^p/\gamma^1)_E$ at $x_c = 0.55$.

Deviation from ideal behavior can have a physical origin such as the difference in the intermolecular forces, or a chemical one such as compound formation.[3,20] The former generally leads to positive deviations from Raoult's law and activity coefficients greater than unity, while complexing favors negative deviations and activity coefficients less than unity. As pressure decreases the molecular separations, a change in non-ideality is probable. In an ideal mixture, the components usually are similarly sized molecules with similar force fields, and the ideality should therefore be affected little by an increase in pressure. The system, C_6H_6-CCl_4, fits into this category; the Lennard-Jones potential parameters for the pure components are similar[21] and the molecules are relatively symmetric. The system is relatively ideal at 1 atm. and 25°C[10], and both sets of compressibility data[5,8] indicate little change in the activity coefficients at elevated pressures. Though the properties of pure benzene and cyclohexane are quite well fitted by similar LJ potentials,[21] the structures of the molecules are sufficiently different for significant departure from ideality to occur in mixtures at 1 atm.[9,10] The activity coefficients are increased by up to 4% by a pressure of 300 atm. The system, C_6H_6-$C_2H_4Cl_2$, behaves more ideally than C_6H_6 - C_6H_{12} at 1 atm.,[10] but shows slightly larger pressure dependence. C_6H_6 - $C_6H_5NH_2$ is the least ideal at 1 atm.[13-15] of the four benzene systems we have examined, and this behavior is readily, if not correctly, attributed to the polarity of the aniline. However, as the pressure increases, the activity coefficients decrease. The slight increase in ideality is apparently due to Van der Waal's forces becoming more comparable with polar interactions.

The behavior of the remaining aniline systems in which both components are polar differs from that of $C_6H_5NH_2$ - C_6H_6. Aniline and chlorobenzine are similar in size, structure and dipole moment.[22] Of all the systems we have considered, this one shows the largest positive deviation from ideality (i.e., the largest activity coefficients) at 1 atm. The effect of pressure is to cause a small increase–a maximum of 4% at 1400 atm. Nitrobenzene is very strongly polar[22] and the system, $C_6H_5NH_2$ - $C_6H_5NO_2$, is complicated by loose complex formation. Unfortunately, the activity coefficients in this system have not been measured, but negative deviation from Raoult's law has been reported.[23] Gibson and Loeffler commented on the formation of a deep orange color on mixing the pure components, but considered that the small absorption of heat and the expansion of volume on mixing argued against compound formation in the usual sense.[6,7] Considerable work on this system has been carried out by Russian investigators (see Chem. Abs. 1958–1969) and there is overwhelming evidence that an electrondonor-acceptor complex is formed. However, the evidence is conflicting as to whether 1:1 or 2:1 charge transfer complexing takes place.[23,24] However, if a loose compound formation of this type causes the negative deviation from Raoult's law, the effect of pressure should decrease the activity coefficients as occurs in the $CHCl_3$ - Et_2O system. However, in Table I and Figure 2. we see the opposite effect. It can also be argued that if a small volume expansion accompanies the complex formation, an increase in pressure would inhibit this formation and increase the activity coefficients as is seen. Contrary to this argument, Gibson and Loeffler observed that an increase in pressure pushed light absorption farther towards the red and Δv became less positive. Clearly in this system we are confronted with unusual behavior which warrants further investigation but this is outside the scope of the present work.

A more thorough treatment of the $CHCl_3$ - Et_2O system (and perhaps also $PhNH_2$ - $PhNO_2$) is afforded by the model of Harris and Prausnitz[25] which takes into account both chemical interactions between the two components and physical forces between the two components and the complex. This treatment requires the equilibrium constant for complex formation, K and a physical interaction parameter, α. The change in the activity coefficients with pressure in solvating binary systems can be considered as two contributions: (i) the change in the equilibrium yield of the solvation product with increasing pressure, and (ii) the usual changes associated with physical effects. As we have seen, the latter changes which we can express through the change in α are usually positive and are comparatively small, whereas the change in the ACR is significant, suggesting that so also is the change in the equilibrium yield. This, of course, would be obvious in the vapor phase since A and B combine to form an AB complex. The system, $PhNH_2$-$PhNO_2$, would be difficult to describe completely, especially if one were to consider the simultaneous effect of both pressure and temperature on the two possible complexing mechanisms. For the time being, we have been content to examine the "apparent" activity coefficients of the parent components, which are the experimentally accessible quantities,[3] and their change with pressure.

8. CONCLUSION

We have verified the feasibility of obtaining the activity coefficients of the components of binary solutions under pressure from PVT data. The numerical evaluation has been carried out in at least two ways for seven systems to check the mathematical consistency of the method. Given a limited amount of composition data, fitting the molar volume at each isobar as a power series in the mole fraction of one component, then integrating with respect to pressure at constant composition proved to be convenient and successful. The accuracy of these calculations is of course dependent on the accuracy of the original PVT data. Since high precision was obtained by both Holder and Whalley[5] and Gibson and Loeffler,[6] it is probable that little additional uncertainty is introduced above that which exists in the estimation of the activity coefficients at 1 atm. The data of Dolezalek and Speidel[8] are much less accurate and more uncertainty must be attached to the ACR's calculated from their results. However, the smoothing of the various isobars and the subsequent integration tend to eliminate random errors in the data and the agreement between the two sets of results for benzene-carbon tetrachloride is satisfactory. The results obtained are physically realistic and have been interpreted briefly in terms of current knowledge of solution behavior.

A consideration of temperature effects, investigation of aqueous and alcohol systems where solvation is provable and an extension of the Harris-Prausnitz model of physical and chemical interactions in binary systems[25] to include the effect of pressure would seem to be profitable.

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