convenient, and accurate method of determining hindrance factors for nonsorbing species in stream beds. In operation it serves as a close physical analogue for the process it models.

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NOTATION

A = subscript that refers to potassium chloride
B = subscript that refers to water
C = total molar concentration, moles/cm^3
C_A, C_B = molar concentration, moles/cm^3
D_{AB} = diffusivity of potassium chloride through water, cm^2/s
D_{AE} = effective diffusivity of potassium chloride through a settled soil slurry, cm^2/s

$$D_{\text{int}} = \frac{1}{C_{A2}^* - C_{A0}} \int_{C_{A0}}^{C_{A2}^*} \frac{D_{AB}dC_A}{1 - \left[V_A + \frac{N_B}{N_A} V_B\right] C_A}$$

H = hindrance factor
N_A, N_B = molar flux of A and B, moles/cm^2, s
$\tilde{V}_A$, $\tilde{V}_B$ = partial molar volume of A and B, cm^3/g mole
X_A, X_B = mole fraction
X_A^* = mole fraction potassium chloride at saturation
Z = distance in the vertical direction, cm
ϵ_1 = void fraction in the salt phase
ϵ_2 = void fraction of settled soil slurry bed
$*$ = superscript that refers to saturation at solid salt interface
o = subscript referring to cell entrance

LITERATURE CITED

Clack, B. W., "On the Study of Diffusion in Liquids by an Optical Method," *Proc. Physical Soc.*, **36**, 313 (1924).

Geankoplis, C. J., *Mass Transport Phenomena*, Holt, Rinehart and Winston, New York (1972).

Ghai, R. K., H. Erth, and F. A. L. Dullien, *AIChE J.*, **19**, 881 (1973).

Gosting, L. J., "A Study of the Diffusion of Potassium Chloride in Water at 25°C with Gouy Interference Method," *J. Am. Chem. Soc.*, **72**, 4418 (1950).

Greskovich, E. J., "Equilibrium Data for Various Compounds Between Water and Mud," *AIChE J.*, **20**, 1024 (1974).

Harned, H. S., and R. L. Nuttall, "The Differential Diffusion Coefficient of Potassium Chloride in Aqueous Solutions," *J. Am. Chem. Soc.*, **71**, 1460 (1949).

Kenner R. C., Jr., M. S. thesis, "Prediction of the Diffusivity of Potassium Chloride in Aqueous Solutions for Hindered and Unhindered Systems," Bucknell University, Lewisburg, Pennsylvania, (1973).

Neale, G. H., and W. K. Nader, "Prediction of Transport Processes Within Porous Media: Diffusive Flow Processes Within a Homogeneous Swarm of Spherical Particles *AIChE J.*, **19**, 112 (1973).

———, "Creeping Flow Relative to a Fixed Swarm of Spherical Particles," *AIChE J.*, **20**, 530 (1974).

Pommersheim, J. M., E. J. Greskovich, and R. C. Kenner, Jr., "Experimental Determination of Liquid Diffusivity Using Salts in a Stefan Cell," to be submitted to *AIChE J.* (1974).

Pommersheim, J. M., and B. A. Ranck, "Measurement of Gaseous Diffusion Coefficients Using the Stefan Cell," *Ind. Eng. Chem. Fundamentals*, **12**, 246 (1973).

Robinson, R. A., and R. H. Stokes, *Electrolyte Solutions, 2 ed.*, Butterworth, London (1970).

Satterfield, C. N., *Mass Transfer in Heterogeneous Catalysis*, Mass. Inst. Technol. Press, Cambridge (1970).

Slattery, J. C., *Momentum, Energy and Mass Transfer in Continua*, McGraw-Hill, New York (1972).

Stokes, R. H., "Integral Diffusion Coefficients of Potassium Chloride Solutions for Calibration of Diaphram Cells," *J. Am. Chem. Soc.*, **73**, 3527 (1951).

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Generalized Prediction of Isothermal Compressibilities and an Isothermal Equation of State for Liquid Mixtures

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For design and analysis of liquid systems under high pressures, knowledge of the equation of state is necessary to obtain values of densities and thermodynamic properties. While liquids are not very compressible, at pressures above 100 bar, the density and its derivative, the compressibility, and thermodynamic properties such as enthalpy and entropy can be appreciably different from that at low pressures. Previously (Brelvi and O'Connell, 1972), we had established a corresponding states correlation for pure component compressibilities using only the density and a single characteristic density parameter. This was shown to be highly accurate for compressions of pure liquids at constant temperatures (Brelvi and O'Connell, 1975). The purpose of this work was to examine methods for predicting the compressibilities of liquid mixtures and to establish a method for calculating the densities and compressibilities of mixtures at high pressures by using low-pressure, pure-component quantities only.

There is a rigorous statistical-mechanical theory for isothermal compressibilities based on fluctuation theory (O'Connell, 1971), but this requires values of all correlation functions in the mixture; these are presently unknown functions of density and composition. In the absence of rigorous theory, several approaches can be taken toward predicting properties of mixtures by using pure component data.

Our previous generalized correlation was of the form

$$\ln\,(1 + 1/\rho\kappa_T RT) = -\,0.42704(\tilde{\rho} - 1) + 2.089(\tilde{\rho} - 1)^2 - 0.42367(\tilde{\rho} - 1)^3 \qquad (1)$$

where

$$\tilde{\rho} = \rho v^* \qquad (2)$$

with values of v^* being tabulated (Brelvi and O'Connell, 1972). Additional values are given in Table 1A (Supplementary Material.* This equation is valid to within 5 to 10% for all temperatures and pressures for which $\tilde{\rho} > 1.7$.

There are two ways in which the mixture density can be obtained for use in the theoretical treatments: experimental mixture density and no volume change on mixing; that is

$$\rho = \left[\sum_{i=1} x_i v_i^o \right]^{-1} \qquad (3)$$

where v_i^o is the pure component molar volume.

The mixture characteristic parameter for use in equation (2) with the above choices of density may be determined from several theoretical approaches. We present comparisons for a method which is similar to the one-fluid method described by Leland and Chappelear (1968):

$$v_m^* = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left(\frac{v_i^{*1/3} + v_j^{*1/3}}{2} \right)^3 \qquad (4)$$

where the values of v_i^* were obtained from the previous tabulations (Brelvi and O'Connell, 1972) and from fitting the experimental pure component compressibilities at the temperature of the system.

There are three combinations of the above methods for use in Equation (1). In Tables 1 and 2A,* method 1 uses Equations (3) and (4) with tabulated v_i^*, method 2 uses Equations (3) and (4) with fitted v_i^*, and method 3 uses Equation (4) with experimental liquid densities and fitted v_i^*. The differences in them will depend on the accuracy of the correlation for pure components and the magnitude of the volume of mixing. [We also tried two-fluid and three-fluid methods and the rigorous formula given by O'Connell (1971) using density independent v_i^* but all gave poor results and are not considered in detail here.]

Two final methods for calculating mixture compressibilities are the simple mole fraction and volume fraction averages:

Mole fraction average

$$\kappa_{T_m} = \sum_{i=1}^{n} x_i \kappa_{T_i} \qquad (5)$$

Volume fraction average

$$\kappa_{T_m} = \sum_{i=1}^{n} x_i v_i^o \kappa_{T_i}^o \Bigg/ \sum_{i=1}^{n} x_i v_i^o \qquad (6)$$

The latter was examined by Dolezalek and Speidel (1920), was used by Scatchard (1937) in a study of volume changes on mixing, and was recommended by Rothardt (1957) for adiabatic compressibilities.

TABLE 1. SUMMARY OF COMPARISONS OF PREDICTIVE METHODS AND EXPERIMENTAL DATA FOR ISOTHERMAL COMPRESSIBILITIES OF LIQUID MIXTURES

System type (number)	Number[a] of data	Average absolute deviation in compressibility, %				
		1[b]	2[b]	3[b]	4[b]	5[b]
Nonpolar binary (6)	92	3.8	1.8	1.8	1.4	1.1
Nonpolar ternary (1)	8	4.2	2.6	2.5	1.0	1.3
Nonpolar binary and ternary (2)	15*	9.6	8.2	3.4	0.3	0.5
Polar-nonpolar (2)	35	4.1	1.5	5.5	1.6	1.2
Polar-polar (2)	27	5.7	1.3	2.0	1.3	1.1
	42*	6.0	0.8	1.3	0.7	0.6
Solvating (3)	39	12.4	5.1	8.4	5.5	5.7
	3*	10.1	2.0	4.2	1.8	1.7
Aqueous (1)	7	23.3	12.0	12.3	13.0	34.8
	7*	11.1	6.5	8.3	12.4	21.8
Overall (15)	275	5.9	2.7	3.7	2.5	3.1

[a] Atmospheric pressure data except for *.

[b] Methods 1 to 3 see page 000. Method 4 from Equation (5). Method 5 from Equation (6).

Data on a variety of binary systems with both positive and negative excess volumes are summarized in Table 1 with predictions from the five methods. Included are both high pressure and low pressure systems.

From the results presented we conclude the following.

1. Values of any excess compressibility (relative to simple mixing of pure component values) are normally small so that, except for chloroform-ethyl ether and aqueous ethanol, large deviations do not occur with any of the methods.
2. Except for the aqueous ethanol system, the volume fraction average of the pure component compressibilities is superior to all other methods considered in representing the mixture compressibility, with the mole fraction average also being quite good. (The average deviations are probably well within the experimental uncertainty.)
3. The generalized correlation, Equation (1), is essentially as good as the above methods when characteristic volumes of pure components obtained by fitting their compressibilities at low pressures are used along with no volume change on mixing.

COMPRESSIONS OF LIQUID MIXTURES

As we showed previously (Brelvi and O'Connell, 1975), Equation (1) could be integrated to obtain the change of volume due to a change of pressure at constant temperature. For mixtures, this requires values of the characteristic parameter and of the low-pressure volume. For simple systems there are several possible methods for using pure component quantities which can be tried. (1) The mixture v^* can be obtained from a mixing rule such as the one-fluid method or obtained by fitting the compressibility of the mixture calculated by an average of pure component values, such as the mole fraction average or the

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* See footnote on page 1027.

TABLE 2. SUMMARY OF COMPARISONS OF PREDICTIVE METHODS AND EXPERIMENTAL DATA FOR ISOTHERMAL COMPRESSIONS OF LIQUID MIXTURES

System type (number)	Number of data	Average absolute deviation in fraction volume change, %[a]						
		1[b]	2[b]	3[b]	4[b]	5[b]	6[b]	7[b]
Nonpolar (2)	14	3.9	3.7	3.8	3.3	3.9	3.5	3.5
Polar-polar (2)	27	1.0	1.3	4.0	2.9	0.9	1.9	1.0
Solvating (2)	9	19.1	20.3	6.3	2.0	4.9	2.1	—
Overall nonaqueous (6)	50	5.2[c]	5.4[c]	4.2	2.7	2.5	2.3	—
Aqueous (5)	38	14.0	23.4	13.8	21.2	20.5	10.3	—

[a] Average error in $[v_2(\text{exp}) - v_2(\text{calc})]/[v_2(\text{exp}) - v_1(\text{exp})]$ where the subscript 1 refers to the low pressure and subscript 2 refers to high pressure.

[b] Methods are:

1. Mixture v^* from Equation (4) by using tabulated pure component v^* and ignoring excess volume.
2. Mixture v^* from fit to volume fraction average of pure component compressibilities predicted from pure component densities and tabulated pure component v^* and ignoring excess volume.
3. Method 1 with fitted pure component v^* values.
4. Method 2 by using pure component v^* from fitting pure component compressibilities or compressions.
5. Method 3 by using experimental mixture volume.
6. Method 4 by using experimental mixture volume.
7. Mixture v^* from low pressure mixture compressibility and experimental mixture volume.

[c] Without Acetone-Chloroform System (6 data), values for methods 1 and 2 are 2.1 and 2.2, respectively, better than all other methods.

volume fraction average. (2) The volume of the mixture may be the actual value or the value from assuming no excess volume. (3) The pure component compressibilities can be experimental or predicted from tabulated values of v^*. We made calculations for nine of the combinations of these and present some results for seven methods in Table 2 (extended Table 3A in Supplementary Material). In general, the results for the mixtures are similar to those for pure components when tabulated and fitted values of v^* are used.

The accuracy obtained for various methods with pure component values used divide into aqueous and nonaqueous systems. For nonaqueous systems, all methods give results accurate to within a few percent. Since there is little to choose from in accuracy, it seems that the method which predicts v_m^* from Equation (4) with tabulated pure component v^* values and ignores excess volume is the most convenient. Fitted values of the pure component v^* are slightly more accurate. (In the single case where the results are poor, the pure component data disagree with later work. Thus, the results cited in footnote c of Table 2 are probably more indicative of the accuracy of the method.) For aqueous systems, only three methods (the above methods and one requiring excess volume) yield results that may be acceptable, and these average 10 to 20% errors in fractional volume change. The major reason for the higher errors is because these mixtures are significantly less compressible than the nonaqueous systems. While the most complex method is recommended for aqueous systems, it does require the low-pressure mixture density and a fitting scheme to obtain v_m^* which may not be worth the effort because the average percent error in compressed volume is 0.50 compared to 0.71 for the much simpler method cited above.

While of less practical interest, calculations of the pressure difference given the two volumes yielded percentage errors that were from one to two times the values listed in Table 2. The error in the final volume for nonaqueous systems ranged from five to twenty times less than the errors in compressibility given in Table 1.

Finally, there is a method involving simple measurements which is applicable to complex mixtures where information about pure components may not be known or are too numerous, for example, oils and natural products. The value of v^* can be obtained from a single low-pressure compressibility and density measurement and used to predict compressions under all conditions when the low-pressure density is measured. The success of such a method is implied by column 7 of Table 2 for the systems considered here.

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NOTATION

p = total pressure, bar
R = universal gas constant = 83.143 bar-cm^3/g mole-°K
T = absolute temperature, °K
v = molar volume, cm^3/g mole
v^* = characteristic volume of pure liquid, cm^3/g mole
x = mole fraction
κ_T = isothermal compressibility
ρ = molar density
$\tilde{\rho}$ = reduced density = ρv^*

Superscripts

o = pure component
$'$ = low pressure
$''$ = high pressure

Subscripts

m = mixture

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LITERATURE CITED

Brelvi, S. W., and J. P. O'Connell, "Corresponding States Correlations for Liquid Compressibility and Partial Molar Volume of Gases at Infinite Dilution in Liquids," *AIChE J.*, **18**, 1239 (1972).

———, "A Generalized Isothermal Equation of State for Dense Liquids," *ibid.*, **21**, 171 (1975).

Dolezalek, F., and F. Speidel, "The Theory of Binary Mixtures VI. The Compressibility of Binary Mixtures," *Z. Physik. Chem.*, **94**, 72 (1920).

Gibson, R. E., "The Influence of the Concentration and Nature of the Solute on the Compressions of Certain Aqueous Solutions," *J. Am. Chem. Soc.*, **57**, 284 (1935a).

———, "The Compressions and Specific Volumes of Aqueous Solutions of Resorcinol and Methanol at 25° and the Behavior of Water in These Solutions," *ibid.*, **57**, 1551 (1935b).

Leland, T. W., and P. S. Chappelear, "The Corresponding States Principle," in *Applied Thermodynamics*, p. 83, American Chemical Society, New York (1968).

Newitt, D. M., and K. E. Weale, "Pressure-Volume-Temperature Relations in Liquids and Liquid Mixtures, Part II. The Compression Isotherms of Some Organic Liquids Up to 1000 Atmospheres and Compressions of Some Aqueous and Non-Aqueous Binary Liquid Mixtures," *J. Chem. Soc.* (*London*), 3095 (1951).

O'Connell, J. P., "Thermodynamic Properties Based on Correlation Functions," *Mol. Phys.*, **20**, 27 (1971).

Rothardt, C., "On the Additivity of the Adiabatic Compressibility in Binary Liquid Mixtures," *Z. Physik. Chem.* (*Liepzig*), **206**, 299 (1957).

Scatchard, G., "Change of Volume on Mixing and the Equations for Non-Electrolyte Mixtures," *Trans. Faraday Soc.*, **33**, 160 (1937); see also Hildebrand, J. H., and R. L. Scott, *Regular Solutions*, 3 ed., Dover, p-140 (1964).

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The Influence of Polymer Conformation on Turbulent Drag Reduction

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In recent years the search for more efficient turbulent drag reducers has motivated a number of interesting studies on molecular conformation and flexibility (Balakrishnan and Gordon, 1975; Banijamili et al., 1974; Frommer et al., 1974; Hand and Williams, 1970; Kim et al., 1973; Liaw et al., 1971; Parker and Hedley, 1972). Many of these studies have utilized polyelectrolytes, for which conformational changes may easily be induced by variations in solution *p*H or addition of electrolyte. It has been shown that procedures which increase molecular expansion, as reflected, for example, by an increased solution viscosity, generally lead to enhanced drag reducing ability (Balakrishnan and Gordon 1975; Banijamili et al., 1974; Frommer et al., 1974; Kim et al., 1973; Parker and Hedley, 1972). Here we present additional experimental evidence supporting this concept and discuss the complicating effect of elevations in solution viscosity for highly extended molecules. The data also suggest the intriguing possibility that drag reduction experiments may be utilized to infer the presence of intramolecular hydrogen bonding in solution.

EXPERIMENTAL

Aqueous solutions of two commercially available polyelectrolytes were studied: Separan AP273 (Dow Chemical), a polyacrylamide which has undergone approximately 30% hydrolysis, and Versicol S25 (Allied Colloids), a polyacrylic acid. The solution concentrations were 10 and 20 p.p.m. by weight, respectively. According to the manufacturers, both polymers have extremely large molecular weights, about 10^7.

Pressure drop and flow rate measurements were made with a once-through flow system containing a Moyno pump (Robbins and Myers) and a 1.092 cm I.D. stainless steel tube [data for 0.457 and 2.146 cm I.D. tubes are also available (White, 1975)]. Pressures were determined manometrically, and flow rates were obtained by collecting the fluid over a given time interval. Fluid temperatures were approximately 22° to 23°C. Data on water agreed within 3% with accepted friction factor–Reynolds number correlations for smooth tubes.

Solution viscosities were measured with a Wells-Brookfield semimicro viscometer (Brookfield Engineering), at a polymer concentration of 200 p.p.m. by weight and a shear rate of $115 s^{-1}$. Viscosity values at the concentrations utilized in the drag reduction experiments could not be obtained with the Wells-Brookfield viscometer due to the presence of undissolved gellike particles nor could these values be calculated from the friction factor data, since these did not extend far enough into the laminar region.

RESULTS AND DISCUSSION

The polymer solution viscosities are presented in Table 1 for deionized water, high and low *p*H, and with added salt. Although these data are for 200 p.p.m. by weight, it is anticipated that they also reflect conformational changes occurring at the lower concentration levels of interest in drag reduction. Similar findings with regard to the influence of *p*H on viscosity for polyacrylic acid, but at much lower concentration levels, have been reported by Kim et al. (1973). Both polymers exhibit maximum viscosities at intermediate pH levels, where pendant —COO^- groups would be expected to show greatest ionization. At high *p*H values, obtained with sodium hydroxide addition, the excess electrolyte is believed to shield the carboxyl groups from one another, ultimately reducing coil expansion. Viscosity reduction at low *p*H (hydrochloric acid addition) occurs through suppression of COOH ionization. Some work with polyacrylic acid also suggests

TABLE 1. SUMMARY OF POLYMER SOLUTION VISCOSITY DATA

Polymer	Solution	Viscosity @ 200 p.p.m. by weight and 25°C, shear rate $= 115 s^{-1}$
Separan AP273	Deionized water (*p*H ~ 8.6)	0.0086 Ns/m^2
	High *p*H (*p*H = 11.5)	0.0058
	0.1 M NaCl	0.0020
	Low *p*H (*p*H = 3.5)	0.0025
Versicol S25	Deionized water (*p*H ~ 8.1)	0.0105 Ns/m^2
	High *p*H (*p*H = 11.5)	0.0070
	0.1 M NaCl	0.0025
	Low *p*H (*p*H = 3.5)	0.0013