Kidnay (13) for the N_2 + CH_4 + CO_2 system.

Glossary

a	equation of state parameter
b	equation of state parameter
c	equation of state parameter
P	total pressure
R	gas constant
T	temperature
V	molar volume
X	liquid-phase mole fraction
Y	vapor-phase mole fraction

Literature Cited

(1) Cosway, H. F., Katz, D. L., AIChE J., 5, 46 (1959).
(2) Chang, S.-D., Lu, B. C.-Y., Chem. Eng. Prog., Symp. Ser., 63, (81), 18 (1967).
(3) Lu, B. C.-Y., Yu, P., Poon, D. P. L. Nature (London), 222(5195), 768 (1969).
(4) Yu, P., Elshayal, I. M., Lu, B. C.-Y., Can. J. Chem. Eng., 47, 495 (1989).
(5) Barsuk, S. D., Benyaminovich, O. A., Gazov. Promst., 12, 38 (1973).
(6) Hiza, M. J., Kidnay, A. J., Miller, R. C., "Equilibrium Properties of Fluid Mixtures: A Bibliography of Data on Fluids of Cryogenic Interest", NSRDS Bibliographic Series, IFI/Plenum, New York, 1975.
(7) Wichterle, I., Linek, J., Hala, E., "Vapor-Liquid Equilibrium Data Bibliography", Elsevier, New York, 1973; Supplement I, 1976.
(8) Oelrich, L. R., Plöcker, U. J., Knapp, H., "Vapor-Liquid Equilibria, A Bibliography of Published Data of Multicomponent Systems Containing Components with Normal Boiling Points Lower Than 350 K", Institute of Thermodynamics, Technical University of Berlin, Internal Publication, Sept 1977.
(9) Hiza, M. J., Miller, R. C., Kidnay, A. J., J. Phys. Chem. Ref. Data, 8, 799 (1979).
(10) Soave, G., Chem. Eng. Sci., 27, 1197 (1972).
(11) Redlich, O., Kwong, J. N. S., Chem. Rev., 44, 233 (1949).
(12) Peng, D., Robinson, D. B., Ind. Eng. Chem. Fundam., 15, 59 (1976).
(13) Somait, F., Kidnay, A. J., J. Chem. Eng. Data, 23, 301 (1978).
(14) Goodwin, R. D., Roder, H. M., Straty, G. C., NBS Tech. Note (U.S.), No. 684, (1976).
(15) Meyers, C. H., Van Dusen, M. S., J. Res. Natl. Bur. Stand. (U.S.), 10, 381 (1933).
(16) Grausø, L., Fredenslund, A., Mollerup, J., Fluid Phase Equilib., 1, 13 (1977).
(17) Stryjek, R., Chappelear, P. S., Kobayashi, R., J. Chem. Eng. Data, 19, 59 (1976).
(18) Ellington, R. T., Eakin, B. E., Parent, J. D., Gami, D. C., Bloomer, O. T., "Thermodynamic Properties of Gases, Liquids, and Solids", American Society of Mechanical Engineers, Heat Transfer Division, McGraw-Hill, New York, 1959, p 180.
(19) Graboski, M. S., Daubert, T. E., Ind. Eng. Chem. Process Des. Dev., 17, 443, 448 (1978).
(20) Elshayal, I. M., Lu, B. C-Y, Can. J. Chem. Eng., 51, 76 (1973).
(21) Hamam, S. E. M., Lu, B. C-Y., Chem. Eng. J. (Lausanne), 15, 121 (1978).
(22) Stryjek, R., Chappelear, P., Kobayashi, R., J. Chem. Eng. Data, 19, 334 (1974).
(23) Kidnay, A. J., Miller, R. C., Parrish, W. R., Hiza, M. J., Cryogenics, 15, 531 (1975).

Densities and Refractive Indexes of Binary Mixtures in the System Methyl Isobutyl Ketone–2-Butanol. Mathematical Relations Obtained

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Densities and refractive indexes were determined for binary mixtures of methyl isobutyl ketone–2-butanol at temperatures of 20, 25, 30, and 35 °C and at atmospheric pressure. An empirical relation between density, composition, and temperature and, on the other hand, an empirical relation between refractive index, composition, and temperature of the mixture were obtained. The properties of the mixtures predicted through empirical relations were found to be in fairly good agreement with the experimental data and to have validity over the temperature range 20–35 °C.

One need of much importance is the measurement of properties of binary mixtures at different temperatures. To facilitate the interpolation of the data, we derived equations in which the effects of temperature and composition were incorporated.

Materials. Methyl isobutyl ketone (analytical reagent, Merck, Darmstadt) was distilled, refluxed, and fractionated. The fraction boiling between 115 and 116 °C was collected and used in the experimental measurements (2). 2-Butanol (analytical reagent, Merck, Darmstadt) was used without further purification and drying (2). The physical properties of the substances used were compared with corresponding data reported in the literature (Table I).

Experimental Section

Solutions of different composition of the binary system methyl isobutyl ketone–2-butanol were prepared by weight in ground-glass-joint conical flasks by using a Mettler balance H-311 with

Table I. Properties of Methyl Isobutyl Ketone and 2-Butanol

material	temp, °C	density, g cm⁻³ present work (exptl)	density, g cm⁻³ lit	refractive index present work (exptl)	refractive index lit
methyl isobutyl ketone	20	0.8010	0.8008 (1, 2)	1.395 76	1.3962 (4)
	25	0.7963	0.7961 (2)	1.393 61	1.3933 (2)
	30	0.7920		1.391 45	
	35	0.7868		1.389 29	
2-butanol	20	0.8066	0.8063 (4)	1.397 06	1.3974 (4)
	25	0.8025	0.8026 (2)	1.395 30	1.3950 (2)
	30	0.7987		1.393 42	
	35	0.7938		1.391 55	

an accuracy of ±0.0005 g. The densities were obtained with a Robertson specific gravity bottle (3) with an accuracy of ±0.0001 g cm⁻³. In making determinations, we maintained the pycnometer in a bath until two consecutive measurements of the liquid height in the capillary indicated that the sample had reached the temperature of the bath.

Refractive indexes for the sodium D line of the pure components and mixtures were measured with a Jena dipping refractometer with an accuracy of ±0.00002. In both cases, a thermostatically controlled bath, constant to 0.01 °C, was used.

Results and Discussion

The density data at 20, 25, 30, and 35 °C for the system methyl isobutyl ketone–2-butanol are given in Table II. The

Table II. Density Data for the Mixtures at 20, 25, 30, and 35 °C

X_{Mik}	20 °C			25 °C		
	ρ_{exptl}	ρ_{calcd}	$10^2 E\%$	ρ_{exptl}	ρ_{calcd}	$10^2 E\%$
0.0000	0.8066	0.8069	3.71	0.8025	0.8026	1.2
0.1009	0.8048	0.8046	2.5	0.8005	0.8001	5.0
0.2015	0.8034	0.8030	5.0	0.7992	0.7984	10.0
0.3000	0.8025	0.8019	7.5	0.7981	0.7973	10.0
0.4014	0.8018	0.8012	7.5	0.7970	0.7965	6.3
0.5052	0.8012	0.8009	3.7	0.7964	0.7962	8.8
0.6018	0.8006	0.8008	2.5	0.7962	0.7961	1.3
0.7031	0.8004	0.8009	6.3	0.7959	0.7961	2.5
0.8002	0.8006	0.8009	3.7	0.7956	0.7962	7.5
0.9079	0.8008	0.8009	1.2	0.7960	0.7962	2.5
1.0000	0.8010	0.8007	3.7	0.7963	0.7959	5.0

X_{Mik}	30 °C			35 °C		
	ρ_{exptl}	ρ_{calcd}	$10^2 E\%$	ρ_{exptl}	ρ_{calcd}	$10^2 E\%$
0.0000	0.7987	0.7983	5.0	0.7938	0.7941	3.8
0.1009	0.7966	0.7957	11.3	0.7910	0.7913	3.8
0.2015	0.7949	0.7938	13.8	0.7897	0.7893	5.1
0.3000	0.7938	0.7926	15.1	0.7884	0.7880	5.1
0.4014	0.7930	0.7918	11.3	0.7875	0.7871	5.1
0.5052	0.7924	0.7915	13.3	0.7868	0.7868	0.0
0.6018	0.7917	0.7914	3.8	0.7866	0.7867	1.3
0.7031	0.7916	0.7914	2.5	0.7862	0.7867	6.3
0.8002	0.7915	0.7915	0.0	0.7860	0.7868	10.2
0.9079	0.7917	0.7915	2.5	0.7864	0.7868	5.1
1.0000	0.7920	0.7912	10.1	0.7868	0.7865	3.8

Table III. Refractive Index Data for the Mixtures at 20, 25, 30, and 35 °C

X_{Mik}	20 °C			25 °C		
	$n_{D\,exptl}$	$n_{D\,calcd}$	$10^2 E\%$	$n_{D\,exptl}$	$n_{D\,calcd}$	$10^2 E\%$
0.0000	1.39706	1.39703	0.5	1.39530	1.39530	0.0
0.1028	1.39654	1.39632	1.6	1.39450	1.39428	1.6
0.2131	1.39611	1.39605	0.4	1.39395	1.39396	0.1
0.2934	1.39594	1.39583	0.8	1.39374	1.39368	0.4
0.4034	1.39579	1.39565	1.0	1.39345	1.39346	0.1
0.5008	1.39559	1.39563	0.3	1.39336	1.39343	0.5
0.6013	1.39544	1.39553	0.6	1.39330	1.39333	0.2
0.6991	1.39546	1.39564	1.3	1.39321	1.39345	1.7
0.7979	1.39543	1.39570	1.9	1.39330	1.39353	1.6
0.8998	1.39560	1.39577	1.2	1.39343	1.39360	1.2
1.0000	1.39576	1.39579	0.2	1.39361	1.39364	0.2

X_{Mik}	30 °C			35 °C		
	$n_{D\,exptl}$	$n_{D\,calcd}$	$10^2 E\%$	$n_{D\,exptl}$	$n_{D\,calcd}$	$10^2 E\%$
0.0000	1.39342	1.39347	0.4	1.39155	1.39165	0.7
0.1028	1.39259	1.39226	2.4	1.39063	1.39024	2.8
0.2131	1.39194	1.39187	0.5	1.38987	1.38979	0.6
0.2934	1.39164	1.39154	0.7	1.38943	1.38940	0.2
0.4034	1.39132	1.39127	0.4	1.38912	1.38909	0.2
0.5008	1.39114	1.39122	0.6	1.38901	1.38902	0.1
0.6013	1.39108	1.39113	0.4	1.38885	1.38893	0.6
0.6991	1.39106	1.39126	1.4	1.38886	1.38901	1.1
0.7979	1.39117	1.39135	1.3	1.38891	1.38918	1.9
0.8998	1.39131	1.39145	1.0	1.38906	1.38929	1.6
1.0000	1.39145	1.39149	0.3	1.38929	1.38934	0.4

Figure 1. Mixture densities vs. temperature.

Figure 2. B constant in eq 1 vs. molar fraction of methyl isobutyl ketone.

Figure 3. A vs. B constants in eq 1.

refractive index data for this system are given in Table III. The following functional relationship between densities of the mixtures and temperature was assumed:

$$\rho = A e^{Bt} \tag{1}$$

Density data of the mixture are plotted against t in Figure 1, keeping the molar fraction of methyl isobutyl ketone as a pa-
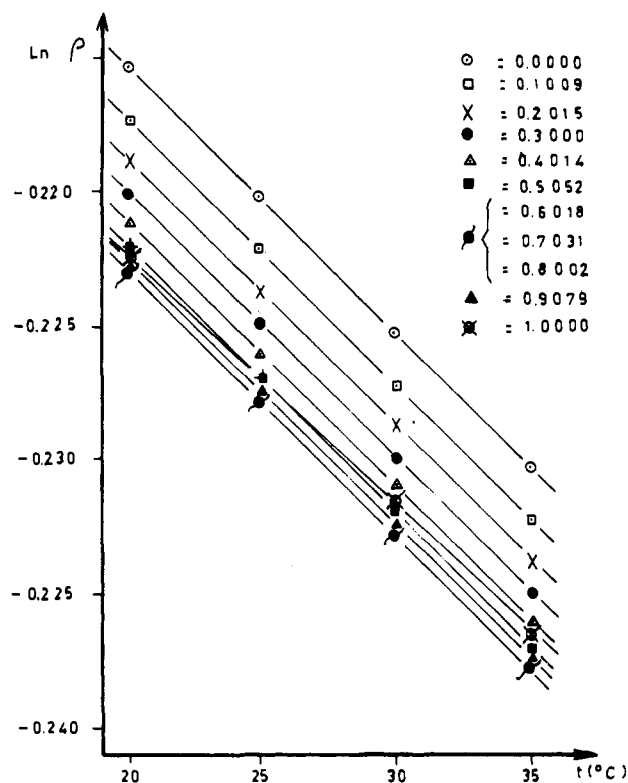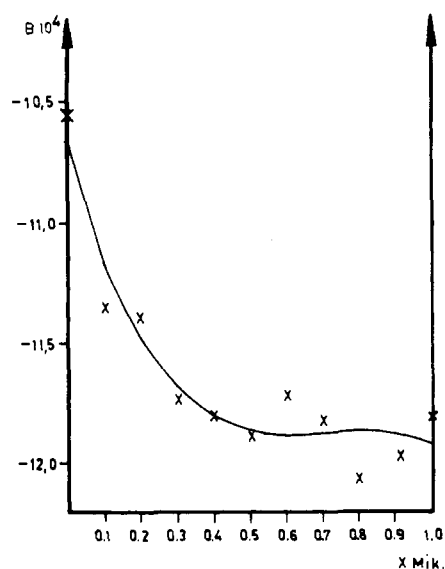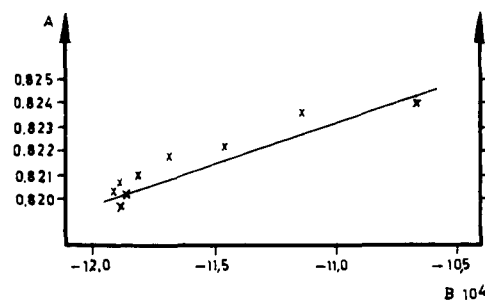
rameter, which resulted in a linear plot for each of the integral values of composition as stated above. From these data, the

following relation between B and X was found (Figure 2):

$$B = (-10.67 - 5.35X + 7.65X^2 - 3.56X^3) \times 10^{-4}$$

$$\sigma_B = 4.034 \times 10^{-5} \quad (2)$$

Further, another relationship between A and B (Figure 3) is given by

$$A = 0.8607 + 34.125B$$

$$\sigma_A = 1.377 \times 10^{-3} \quad (3)$$

The following equation was obtained:

$$\rho = [(8243.08 - 182.55X + 261.21X^2 - 121.39X^3) \times 10^{-4}] \exp[t(-10.67 - 5.35X + 7.65X^2 - 3.56X^3) \times 10^{-4}] \quad (4)$$

For the refractive indexes, the following equation was assumed:

$$n_D = A'e^{B't} \quad (5)$$

The work of calculation was made in a similar form as described before, and the following results were obtained:

$$B' = (-2.62 - 2.45X + 3.48X^2 - 1.50X^3) \times 10^{-4}$$

$$\sigma_{B'} = 1.694 \times 10^{-5} \quad (6)$$

$$A' = 1.4046 + 0.5B'$$

$$\sigma_{A'} = 0.000 \quad (7)$$

Equation 8 was obtained to relate the refractive index to the temperature and composition of the mixture.

$$n_D = [(14044.69 - 1.23X + 1.74X^2 - 0.75X^3) \times 10^{-4}] \exp[t(-2.62 - 2.45X + 3.48X^2 - 1.50X^3) \times 10^{-4}] \quad (8)$$

In this case the relationship between B' and X becomes slightly curved, owing to the relative importance of the association between the components of the mixture.

By means of eq 4 and 8, density and refractive index data at any given temperature and composition within the experimental ranges can be predicted. Density and refractive index data predicted through eq 4 and 8 compare well with experimental data (Tables II and III), and the average percent deviations are 5.5×10^{-2} and 0.8×10^{-2}, respectively.

Glossary

A, B	constants in eq 1
A', B'	constants in eq 5
ρ	density of the mixture, g cm^{-3}
n_C	refractive index
X_{Mk}	molar fraction of methyl isobutyl ketone
t	temperature, °C
E	error percentage
σ_B, σ_A, $\sigma_{B'}$, $\sigma_{A'}$	standard deviations for eq 2, 3, 6, and 7, respectively

Literature Cited

(1) Janz, G. J.; Tomkins, R. P. T. "Nonaqueous Electrolytes Handbook"; Academic Press: New York, 1972; Vol. I.
(2) Riddic, J. A.; Bunger, W. B. "Organic Solvents", 3rd ed.; Wiley-Interscience: New York, 1970; Vol. II.
(3) Robertson, G. R. *Ind. Eng. Chem., Anal. Ed.* 1939, 11, 464.
(4) Weast, J. "Handbook of Chemistry and Physics", 58th ed.; C.R.C. Press: Cleveland, OH, 1977.

Thermodynamic Studies of the Interactions of Guanidinium Chloride with Some Oligopeptides Containing L-Valine, L-Leucine, L-Tryptophan, and L-Tyrosine

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The solubilities of several oligopeptides containing L-valine, L-leucine, L-tryptophan, and L-tyrosine have been measured in water and guanidinium chloride solutions. Approximate Gibbs free energies of transfer of peptide backbone units and valyl, tryptophyl, and tyrosyl side chains from water to guanidinium chloride solutions have been calculated. Enthalpies of transfer for the same groups have been determined from calorimetric measurements. The results obtained show that the behavior of the aromatic side chains in guanidinium chloride solutions is fundamentally different from that of the aliphatic side chains. For the latter the entropic contributions to Gibbs free energies of transfer are relatively large; for the former they are relatively small. The difference in behavior indicates in all probability that aliphatic side chains interfere more strongly than aromatic ones with the structure of the solvent surrounding them.

In a previous paper we reported on the determination of thermodynamic quantities, i.e., changes of Gibbs free energy and enthalpy, for the transfer of oligoglycines and oligoleucines from water to guanidinium chloride and urea solutions of various concentrations (*1*). Both compounds are strong protein denaturants; i.e., they produce partial or complete unfolding (*2*). The results obtained in studies of oligopeptides should help in interpreting the values of the thermodynamic quantities of proteins for the same transfers. It is evident that in the case of proteins the transfer is a more complex process, involving not only unfolding but also large solvation changes. The latter contribute essentially to the thermodynamic quantities of transfer (*3*). Practically the only way to ascertain these contributions is to study oligopeptides of properly selected compositions.

In this report the results obtained are presented in studies of transfer of several oligopeptides containing L-valine, L-leucine, L-tryptophan, and L-tyrosine from water to guanidinium chloride solutions. The procedure for determination of the thermodynamic