sols in the Size Range of 0.01 to 0.25 Microns Diameter. *J. Colloid Sci.* **1974**, *5*, 471–496. (b) Lewis, G. N.; Randall, M. *Thermodynamics and the Free Energy of Chemical Substances*, 1st ed.; McGraw-Hill: New York, 1926; p 554.
(31) Lisle, E. S.; Sensenbaugh, J. D. The Determination of Sulfur Trioxide and Acid Dew Point in Flue Gases. *Combustion* **1965**, *36*, 12–16.
(32) Luchinskij, G. P. Physical-Chemical Study of the H_2O–SO_3 System. *Zh. Fiz. Khim.* **1956**, *30*, 1207–1221.
(33) Middleton, P.; Kiang, C. S. Experimental and Theoretical Examination of the Formation of Sulfuric Acid Particles. *Atmos. Environ.* **1978**, *12*, 179–185.
(34) Mirabel, P.; Katz, J. L. Binary Homogeneous Nucleation Mechanism for the Formation of Aerosols. *J. Chem. Phys.* **1974**, *60*, 1138–1144.
(35) Myers, T. What is the Boiling Point and Heat of Vaporization of Sulfuric Acid? *J. Chem. Educ.* **1983**, *60*, 1017–1018.
(36) Pilat, M. J.; Wilder, J. M. Opacity of Monodisperse Sulfuric Acid Aerosols. *Atmos. Environ.* **1983**, *17*, 1825–1835.
(37) Roedel, W. Measurement of Sulfuric Acid Saturation Vapor Pressure; Implications for Aerosol Formation by Heteromolecular Nucleation. *J. Aerosol Sci.* **1979**, *10*, 375–386.
(38) Shankman, S.; Gordon, A. R. The Vapor Pressure of Aqueous Solutions of Sulfuric Acid. *J. Am. Chem. Soc.* **1939**, *61*, 2370–2373.
(39) Shugard, W. J.; Heist, R. H.; Reiss, H. Theory of Vapor Phase Nucleation in Binary Mixtures of Water and Sulfuric Acid. *J. Chem. Phys.* **1974**, *61*, 5298–5305.
(40) Staples, B. R. Activity and Osmotic Coefficients of Aqueous Sulfuric Acid at 298.15 K. *J. Phys. Chem. Ref. Data* **1981**, *10*, 779–798.
(41) Stokes, R. H. The Measurement of Vapor Pressures of Aqueous Solutions by Bi-Thermal Equilibration through the Vapor Phase. *J. Am. Chem. Soc.* **1947**, *69*, 1291–1296.
(42) Thomas, S. T.; Barker, W. F. The Partial Pressures of Water Vapour and of Sulphuric Acid Vapour over Concentrated Solutions of Sulphuric Acid at High Temperature. *J. Chem. Soc., Trans.* **1925**, *127*, 2824–2831.
(43) Verhoff, F. H.; Banchero, J. T. A Note on the Equilibrium Partial Pressures of Vapors above Sulfuric Acid Solutions. *AIChE J.* **1972**, *18*, 1265–1268.
(44) Vermeulen, T.; Dong, J.; Robinson, S.; Nguyen, T. Vapor-Liquid Equilibrium of the Sulfuric Acid-Water System. AIChE Meeting, Anaheim, CA, June 10, 1982.
(45) Washburn, E. W., Ed. *International Critical Tables*; McGraw-Hill: New York, 1928; Vol. III, pp 302–303.
(46) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 62nd ed; CRC: Boca Raton, FL, 1981.
(47) Wilder, J. M.; Pilat, M. J. Calculated Droplet Size Distributions and Opacities of Condensed Sulfuric Acid Aerosols. *APCA J.* **1983**, *33*, 858–863.

Received for review April 10, 1987. Revised February 27, 1989. Accepted August 23, 1989. We gratefully acknowledge the support of this work by the National Institute of Environmental Health Sciences (Grant No. ES 02429).

Vapor–Liquid Equilibria at 100 kPa for Propionic Acid + Carbon Tetrachloride or 2-Butanone

Masahiro Kato,* Masato Yamaguchi, and Hiroshi Yoshikawa

Department of Industrial Chemistry, Faculty of Engineering, Nihon University, Koriyama, Fukushima 963, Japan

Vapor–liquid equilibria were measured for the two binary systems made of propionic acid + carbon tetrachloride or 2-butanone at 100 kPa of pressure by the dew-point–bubble-point temperature method. Vapor–liquid equilibrium diagrams were obtained without using any analytical instrument by combining the experimental dew-point and bubble-point temperature curves. The experimental data were correlated with the Wilson equation, accounting for the dimerization effect of propionic acid in the vapor phase.

Introduction

In the present study, vapor–liquid equilibria (VLE) were measured for the two binary systems made of propionic acid with carbon tetrachloride or 2-butanone at 100 kPa of pressure by the dew-point–bubble-point apparatus recently modified by M.K. (*1*), without using any analytical instrument. For carbon tetrachloride + propionic acid, two sets of data are available in the literature (*2*, *3*), but large differences are seen between them. New reliable data seem, therefore, to be required for this system. For 2-butanone + propionic acid system, isothermal data are available in literature but no isobaric data.

Experimental Section

The experimental apparatus and procedures were as described in our previous paper (*1*). Temperature was measured by means of a Hewlett-Packard Model 2804A quartz thermometer with an accuracy of 0.01 K. The solutions of desired composition were prepared with an accuracy of 0.001 in mole

Table I. Densities ρ and Normal Boiling Points T_b of the Materials Used

	ρ(298.15 K)/(g cm^{-3})		T_b/K	
material	exptl	lit. (*9*)	exptl	lit. (*9*)
carbon tetrachloride	1.5845	1.584 62	349.84	349.788
2-butanone	0.7995	0.799 7	352.72	352.79
propionic acid	0.9879	0.988 06	414.01	414.315

Table II. Experimental Dew-Point T_d and Bubble-Point T_b Data for the Carbon Tetrachloride (1) + Propionic Acid (2) System at 100 kPa as a Function of the Mole Fraction x_1 of Carbon Tetrachloride

x_1	T_d/K	T_b/K	x_1	T_d/K	T_b/K
0.000		413.59	0.500	389.64	360.34
0.050		401.24	0.600	384.05	357.26
0.100	409.55	391.28	0.700	377.63	354.55
0.200	404.82	377.78	0.800	369.84	352.56
0.300	400.07	370.04	0.900	360.50	350.78
0.400	395.18	364.16	1.000		349.41

Table III. Experimental Dew-Point T_d and Bubble-Point T_b Data for the 2-Butanone (1) + Propionic Acid (2) System at 100 kPa as a Function of the Mole Fraction x_1 of 2-Butanone

x_1	T_d/K	T_b/K	x_1	T_d/K	T_b/K
0.000		413.59	0.500	393.92	370.83
0.050		407.57	0.600	388.68	366.15
0.100	411.10	402.39	0.700	382.70	361.98
0.200	407.30	392.64	0.800	375.71	358.34
0.300	403.26	384.14	0.900	367.04	355.21
0.400	398.89	377.25	1.000		352.30

0021-9568/90/1735-0085$02.50/0

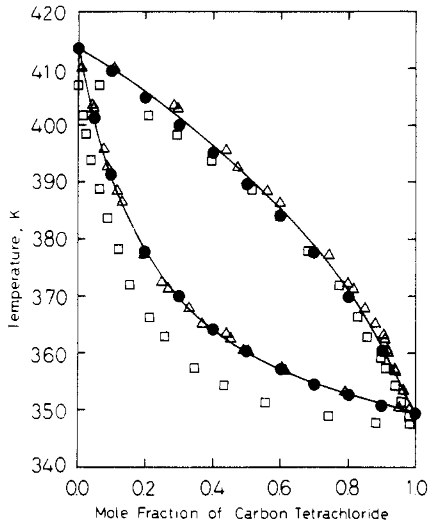

Figure 1. Experimental dew-point–bubble-point temperatures for the carbon tetrachloride + propionic acid system: (●) this work, 100 kPa; (—) Wilson equation, 100 kPa; (△) Wisniak–Tamir (*2*), 101.33 kPa; (□) Paul (*3*), 94.66 kPa.

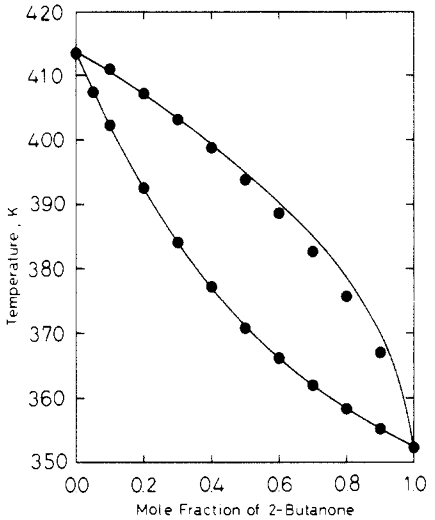

Figure 2. Experimental dew-point–bubble-point temperatures for the 2-butanone + propionic acid system: (●) this work, 100 kPa; (—) Wilson equation, 100 kPa.

fraction by use of an automatic balance.

Special-grade reagents were supplied by Wako Pure Chemical Industries, Ltd. Propionic acid and 2-butanone were purified by fractional distillation in a 30-plate Oldershaw column. Carbon tetrachloride was used without further purification. The physical properties of the materials used are listed in Table I.

Results

The experimental dew- and bubble-point data are given in Tables II and III and shown in Figures 1 and 2. For the carbon tetrachloride + propionic acid system, large differences exist among the literature data (*2*, *3*). The present experimental data compare fairly well with the data of Wisniak–Tamir (*2*). When a comparison is made with the data of Paul (*3*), a substantial difference is seen between the liquid compositions and no difference in the vapor compositions. Wisniak–Tamir (*2*) determined the equilibrium compositions with the refractive index measurements. Paul (*3*) obtained the equilibrium compositions with the titration technique. The present experimental data were obtained without using any analytical instrument. As shown in Figure 1, the VLE data reported by Paul (*3*) seem doubtful. For the 2-butanone + propionic acid system, isobaric data are not available in the literature.

Table IV. Smoothed Vapor–Liquid Equilibrium Data, Temperature T and Liquid-Phase x_1 and Vapor-Phase y_1 Mole Fractions, for Carbon Tetrachloride (1) + Propionic Acid (2) at 100 kPa

T/K	x_1	y_1	T/K	x_1	y_1
413.59	0.000	0.000	373.00	0.259	0.764
407.00	0.023	0.154	364.00	0.406	0.868
401.00	0.045	0.280	358.00	0.574	0.927
394.00	0.081	0.422	353.00	0.773	0.973
388.00	0.119	0.536	349.41	1.000	1.000
382.00	0.163	0.636			

Table V. Smoothed Vapor–Liquid Equilibrium Data, Temperature T and Liquid-Phase x_1 and Vapor-Phase y_1 Mole Fractions, for 2-Butanone (1) + Propionic Acid (2) at 100 kPa

T/K	x_1	y_1	T/K	x_1	y_1
413.59	0.000	0.000	376.00	0.418	0.795
407.00	0.055	0.210	370.00	0.516	0.868
401.00	0.114	0.355	364.00	0.649	0.932
395.00	0.175	0.480	358.00	0.809	0.976
389.00	0.241	0.595	352.31	1.000	1.000
383.00	0.315	0.694			

Table VI. Wilson Parameters Λ_{ij} and Mean Absolute Deviations in Temperature ΔT and Vapor-Phase Composition Δy_1 Obtained from the VLE Data[a]

system	Λ_{12}	Λ_{21}	ΔT/K	Δy_1
carbon tetrachloride (1) + propionic acid (2)	0.1912	1.0800	0.48	0.010
2-butanone (1) + propionic acid (2)	0.2657	2.0464	0.14	0.024

[a] Λ_{ij} defined in ref 5. $\Delta T = \sum|T_{\mathrm{calc}} - T_{\mathrm{exptl}}|/N$. $\Delta y_1 = \sum|y_{1,\mathrm{calc}} - y_{1,\mathrm{exptl}}|/N$ (N, number of experimental points).

After the experimental dew-point temperature curve and the bubble-point one were combined, smoothed VLE data were obtained as given in Tables IV and V.

The VLE data were correlated with the Wilson equation (*4*), accounting for the dimerization effect of propionic acid in the vapor phase with the calculation procedures given in detail in the Dechema collection (*5*). The Wilson parameters Λ_{ij} (Table VI) were determined to minimize the sum of the squares of the deviations in bubble-point temperatures, all points weighted equally.

The vapor pressures of the pure components have been calculated with the Antoine equation, with coefficients estimated by Boublik et al. (*6*) from direct experimental measurements reported by Boublik (*6*) for carbon tetrachloride, Ambrose et al. (*7*) for propionic acid, and Ambrose et al. (*8*) for 2-butanone. The mean absolute deviations of equilibrium vapor composition and equilibrium temperature between the experimental data and calculated ones are shown in Table VI.

Acknowledgment

We thank Takashi Onosato, Hiroshi Kusaka, and Tomonori Tamura for their help in the present experimental work.

Literature Cited

(1) Kato, M. *J. Chem. Eng. Data* **1988**, *33*, 499.
(2) Wisniak, J.; Tamir, A. *J. Chem. Eng. Data* **1978**, *21*, 88.
(3) Paul, R. N. *J. Chem. Eng. Data* **1976**, *21*, 165.
(4) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
(5) Gmehling, J.; Onken, U.; Grenzheuser, P. *Vapor-Liquid Equilibrium Data Collection*, Chemistry Data Series, Vol. 1, Part 5; Dechema: Frankfurt, 1982.
(6) Boublik, T.; Fried, V.; Hala, E. *The Vapour Pressures of Pure Substances*; Elsevier: Amsterdam, 1984.

J. Chem. Eng. Data **1990**, *35*, 87-93

(7) Ambrose, D.; Ellender, J. H.; Gundry, H. A.; Lee, D. A.; Townsend, R. *J. Chem. Thermodyn.* **1981**, *13*, 795.

(8) Ambrose, D.; Ellender, J. H.; Lees, E. B.; Sprake, C. H. S.; Townsend, R. *J. Chem. Thermodyn.* **1975**, *7*, 453.

(9) *TRC-Thermodynamic Tables-Non-Hydrocarbons*. Thermodynamics Research Center, The Texas A&M University System: College Station, TX, extant 1965 (a-5370); 1974 (a-7240); 1984 (a-5450) (loose-leaf data sheets).

Received for review January 17, 1989. Revised September 18, 1989. Accepted October 2, 1989.

Apparent Molar Volumes and Viscosities of Some α- and α,ω-Amino Acids in Aqueous Ammonium Chloride Solutions at 298.15 K

Meena Natarajan,[†] **Ramesh K. Wadi, and Harish C. Gaur***

Department of Chemistry, University of Delhi, Delhi 110007, India

Apparent molar volumes and viscosity *B* coefficients of some α-, substituted α-, and α,ω-amino acids have been determined in water and aqueous ammonium chloride solutions at 298.15 K with a vibrating-tube digital density meter and a modified Cannon–Ubbelhode suspended-level viscometer. An increase in the volume of transfer of amino acids from water to aqueous ammonium chloride solutions and of viscosity *B* coefficients with increasing electrolyte concentration has been explained due to strong interactions of NH_4^+ and Cl^- with the charged centers of the zwitterions compared to ion–nonpolar-group interactions. The interactions have been rationalized in terms of the cosphere overlap model.

Introduction

Thermodynamic data for amino acids and peptides facilitate interpretation of results of even relatively complex biomolecules where a simple additivity rule is applicable. Volumetric and viscometric properties and changes in enthalpy and free energy give useful information about interactions in solutions and have been used to draw important conclusions regarding protein unfolding (*1*) and the extent of hydrophobic interactions of nonpolar side chains (*2*). Differential affinities of amino acid side chains for water have also been reported (*3*). Salt-induced electrostatic forces are known to play a role in modifying the protein structure (*4*) by affecting properties like solubility, denaturation, and activity of enzymes (*5*, *6*). Amino acids are model compounds for interpretation of the behavior of more complex protein molecules in solution. Their equilibrium properties in solution depend on the relative magnitude of electrostriction caused by the polar end groups, the structure-enforcing influence of the hydrophobic alkyl groups, and the extent of interaction between the hydrophilic and hydrophobic groups. Changes in enthalpy, free energy, and volume have been rationalized in terms of these interactions and have helped in evaluating, interalia, the extent of solvation. For some amino acid–water systems in the presence of salts, the heat capacity and free energy of transfer from aqueous to ionic environment have been reported (*7*, *8*). Recently, Ahluwalia et al. (*9*–*11*) reported apparent molar volumes of amino acids in aqueous salt and carbohydrate solutions. Ogawa, Mizutani, and Yasuda (*12*) and also Sandhu (*13*–*15*) have studied the viscosities and apparent molar volumes of amino acids in mixed aqueous solutions. Partial molar volumes of amino acid mixtures in water have also been reported (*16*).

Since ammonium and alkyl-substituted ammonium salts are known to influence the conformational stability of proteins in solution (*17*), a systematic study of their influence on volumetric and viscometric behavior of a series of amino acids is of current interest. Both these properties are sensitive to specific interactive changes in solution. In this paper, apparent molar volumes and viscosities of some α-, substituted α-, and α,ω-amino acids in ammonium chloride solution are reported.

Experimental Section

The α- and α,ω-amino acids chosen for the study were glycine, DL-α-alanine, DL-α-aminobutyric acid, DL-norvaline, DL-norleucine, β-alanine, γ-aminobutyric acid, δ-aminovaleric acid, and ϵ-aminocaproic acid. The α-amino acids with substituted side chain were L-serine, L-threonine, DL-valine, L-glutamine, DL-methionine, and DL-phenylalanine. All amino acids, obtained from Sigma, were of chromatographic purity and were used after drying at ca. 350 K, followed by vacuum desiccation over P_2O_5 for ca. 48 h. Ammonium chloride (B.D.H, AnalaR) was dried for ca. 72 h at ca. 373 K before use. All solutions were prepared afresh by weight with deionized, double-distilled water degassed by boiling.

Solution densities were measured with an Anton Paar (Model DMA 60/601) vibrating-tube digital density metal with precision of $\pm 3 \times 10^{-6}$ g cm^{-3}. The temperature in the measuring cell was controlled to ±0.01 K and monitored with a Paar Model DT-100-20 digital thermometer. The density meter was calibrated everyday with use of the literature data for densities of dry air (*18*) and water (*19*) at 298.15 K. The partial molar volumes of sodium chloride and ammonium chloride determined with the setup agreed within ±0.5% of the reported values (*20*, *21*). The partial molar volumes of typical amino acids in water also agreed within ±0.5% of the values reported by Jolicoeur (*22*). Density measurements were made on solutions of amino acids in water and also in 0.25, 0.50, 1.25, and 2.00 mol kg^{-1} aqueous NH_4Cl at 298.15 K. The concentration range of amino acids was up to ca. 0.5 mol L^{-1}, except for those with low solubility where it was limited to ca. 0.08 mol L^{-1}.

Viscosities were measured with a modified Cannon–Ubbelhode suspended-level viscometer (efflux time for water, ca. 400 s at 298.15 K) vertically mounted on a brass frame in a water thermostat. The kinetic energy correction term was found to be negligible. Viscosity results of test measurements on 0–2 mol kg^{-1} of ammonium chloride solutions in water agreed within ±0.25% of the literature values (*23*) while the precision of the measurements was $\pm 5 \times 10^{-6}$ g cm^{-1} s^{-1}. Viscosities of so-

---

[†] Present address: Department of Chemistry, Kirori Mal College, University of Delhi, Delhi 110007, India.

* Author for correspondence.

0021-9568/90/1735-0087$02.50/0 © 1990 American Chemical Society