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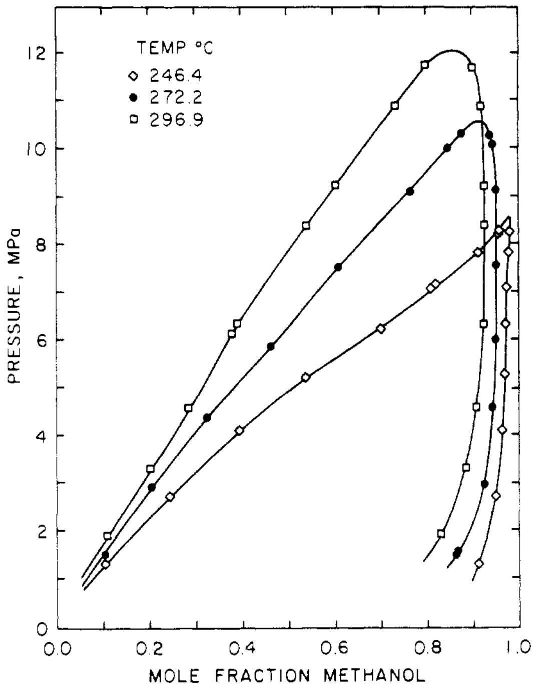

Figure 3. Measured equilibrium pressures and vapor and liquid compositions for 1-methylnaphthalene/methanol mixtures at 246.4, 272.2, and 296.9 °C.

matographic analysis after experimental runs at elevated temperatures.

Results

Vapor and liquid equilibrium compositions have been measured for two binary mixtures: *m*-xylene/carbon dioxide and 1-methylnaphthalene/methanol. Measuremetns of equilibrium pressures and phase compositions for binary *m*-xylene/carbon dioxide mixtures at 202.6 °C have been made for comparison with previously reported data of Robinson and co-workers (*9*). The results obtained in this work are given in Table I, and compared with the existing data in the pressure-composition diagram of Figure 2. The comparison shows very good agreement between our results using the flow experiment and those obtained by Robinson and co-workers using a static method.

Measurements of equilibrium pressures and phase compositions for binary 1-methylnaphthalene/methanol mixtures at 246.4, 272.2, and 296.9 °C are given in Table II and shown in the pressure-composition diagram of Figure 3. The reported compositions represent average values obtained from duplicate samples which are reproducible to within 0.3 mol%. The uncertainties in measured compositions are within 0.1-0.4 mol %. The higher uncertainties are associated with 1-methylnaphthalene compositions greater than 20 mol %.

Mixture critical pressures reported in our results are obtained by observation of critical opalescence and are considered accurate to within ±5 psi. During an experiment, the phase behavior is monitored visually to confirm that equilibrium exists within the cell. Bubbling in the liquid phase or condensation in the gas phase provides definitive indications of perturbations from equilibrium conditions which are evident several minutes before the temperature and pressure readings indicate such phenomena. These visual capabilities become increasingly important for measurements approaching the critical point where such perturbations from equilibrium are more likely to occur. As an additional check for equilibrium conditions, samples were collected for different flow rates at the same operating temperature and pressure. Measured compositions were found to be independent of flow rate, within the experimental uncertainties reported above.

Registry No. Methanol, 67-56-1; 1-methylnaphthalene, 90-12-0.

Literature Cited

(1) Simnick, J. J.; Lawson, C. C.; Lin, H. M.; Chao, K. C. *AIChE J.* **1977**, *23*, 469.
(2) Yao, J.; Sebastian, H. M.; Lin, H. M.; Chao, K. C. *Fluid Phase Equilib.* **1978**, *1*, 293.
(3) Sebastian, H. M.; Nageshwar, G. D.; Lin, H. M.; Chao, K. C. *J. Chem. Eng. Data* **1980**, *25*, 145.
(4) Sebastian, H. M.; Simnick, J. J.; Lin, H. M.; Chao, K. C. *J. Chem. Eng. Data* **1979**, *24*, 149.
(5) Kim, H. Y.; Wang, W.; Lin, H. M.; Chao, K. C. *J. Chem. Eng. Data* **1983**, *28*, 216.
(6) Sebastian, H. M.; Lin, H. M.; Chao, K. C. *J. Chem. Eng. Data* **1981**, *26*, 307.
(7) Kim, H. Y.; Lin, H. M.; Chao, K. C. "Vaporization Equilibrium of Coal Liquids", presented at the Symposium on Thermodynamics and Transport Properties for Synfuel Process Design, Annual AIChE Meeting, Washington, DC, Nov 1983.
(8) Wilson, G. M.; Owens, R. S. "High Temperature Vapor-Liquid Equilibrium Studies on Synthetic Fuel Systems", presented at the Symposium on High Pressure Phase Equilibria—Experimental Data and Methods of Prediction, Annual AIChE Meeting, New York, Nov 1977.
(9) Ng, H. J.; Huang, S. S.; Robinson, D. B. *J. Chem. Eng. Data* **1982**, *27*, 119.

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Solubilities of Cholesterol, Sitosterol, and Cholesteryl Acetate in Polar Organic Solvents

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Solubilities of cholesterol, sitosterol, and cholesteryl acetate are reported at various temperatures ranging from 11 to 50 °C in methanol, ethanol, acetone, acetonitrile, and 2-propanol and in some aqueous mixtures of these solvents. The solubilities of these steroids are represented by best-fit equations for each solvent.

Introduction

It is well-known that cholesterol is an etiologic agent in artherosclerosis diseases (*1*, *2*) while sitosterol lowers cholesterol concentration in the blood (*3*). These diseases are also known to be related to the crystal habit of the two steroids (*4*). In a recent study we have found that the crystal habit is in turn

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Table I. Solubility of Cholesterol in Various Solvents (g/(100 g of solvent))

acetonitrile		methanol		ethanol		acetone		95% ethanol + 5% water		80% ethanol + 20% water		80% acetone + 20% water	
T, °C	*c*	*T*, °C	*c*	*T*, °C	*c*	*T*, °C	*c*	*T*, °C	*c*	*T*, °C	*c*	*T*, °C	*c*
26.0	0.161	20.0	0.648	27.5	3.456	11.0	1.219	20.0	1.546	30.0	0.372	34.0	0.536
30.7	0.187	30.7	0.987	30.7	3.962	30.7	3.752	30.7	2.238	34.6	0.437	39.0	0.711
35.0	0.240	33.9	1.143	33.9	4.445	33.9	4.575	33.9	2.559	39.0	0.589	44.5	1.043
43.0	0.378	40.0	1.510	38.0	5.258	38.0	5.374	38.0	3.006	40.0	0.609		
47.5	0.492	45.0	2.008							44.2	0.811		

Table II. Solubility of Sitosterol in Various Solvents (g/(100 g of solvent))

methanol		ethanol		acetone		95% ethanol + 5% water		80% ethanol + 20% water		80% acetone + 20% water	
T, °C	*c*	*T*, °C	*c*	*T*, °C	*c*	*T*, °C	*c*	*T*, °C	*c*	*T*, °C	*c*
30.4	0.492	30.4	2.901	30.7	4.583	30.4	1.735	29.5	0.160	29.5	0.211
33.9	0.571	33.9	3.504	33.9	4.753	34.0	1.825	34.5	0.215	34.5	0.255
38.0	0.680	38.0	3.901	38.0	5.267	38.0	2.244	38.6	0.318	38.0	0.365
45.3	0.824	42.1	4.628	42.1	6.126	42.1	2.572	44.2	0.440	44.2	0.525
				45.3	7.443						

Table III. Solubility of Cholesteryl Acetate in Various Solvents (g/(100 g of solvent))

methanol		ethanol		2-propanol		acetone		80% ethanol + 20% water		80% acetone + 20% water	
T, °C	*c*	*T*, °C	*c*	*T*, °C	*c*	*T*, °C	*c*	*T*, °C	*c*	*T*, °C	*c*
31.5	0.390	11.5	0.373	11.8	1.230	16.7	5.070	29.5	0.165	29.5	0.193
32.3	0.420	20.5	0.655	20.5	1.911	34.5	11.553	34.5	0.206	34.5	0.289
35.1	0.490	30.0	0.970	30.0	2.827	44.0	19.900	40.0	0.261	39.0	0.370
39.0	0.633	33.0	1.092	33.9	3.612			44.2	0.412	40.0	0.411
41.2	0.689	33.9	1.192	36.5	5.101					44.2	0.585
44.3	0.832	37.5	1.446	37.5	5.138						

affected by the solvent and by the supersaturation values (*5*). In order to determine these values, solubility curves of cholesterol and sitosterol are essential (*6*).

The aims of this study are to obtain solubility data of cholesterol, sitosterol, and cholesteryl acetate in several polar organic solvents at various temperatures and to possibly correlate them by best-fit equations. So far, the available information on the solubility of cholesterol in different solvents is quite scanty (*5*, *7–9*) while there is none on sitosterol and choelsteryl acetate solubilities.

Experimental Section

Cholesterol, sitosterol, and cholesteryl acetate, purchased from Aldrich with 99% purity, were further recrystallized from acetone and kept under nitrogen. The organic solvents—either spectroscopic grade or absolute (alcohols)—were used as such.

Solutions with excess of solids were deeply immersed in a thermostatically controlled water bath (±0.1 °C) and magnetically agitated for 12 h (a much longer time had no effect on the solubilities). After the attainment of saturation equilibrium, the stirring was interrupted for 12 h, after which three aliquots (3–4 mL) of the supernatant clear solution were withdrawn by preheated pipets. The samples were immediately cooled in an ice bath to minimize solvent evaporation and then gravimetrically analyzed (±0.0001 g) before and after careful solvent evaporation.

Results

The measured solubilities, expressed in (g of solute)/(100 g of solvent) for cholesterol, sitosterol, and cholesteryl acetate are shown in Tables I–III, respectively.

The data were fitted by a least-squares method to an equation of the form

$$\log (1/x) = A/T + B \qquad (1)$$

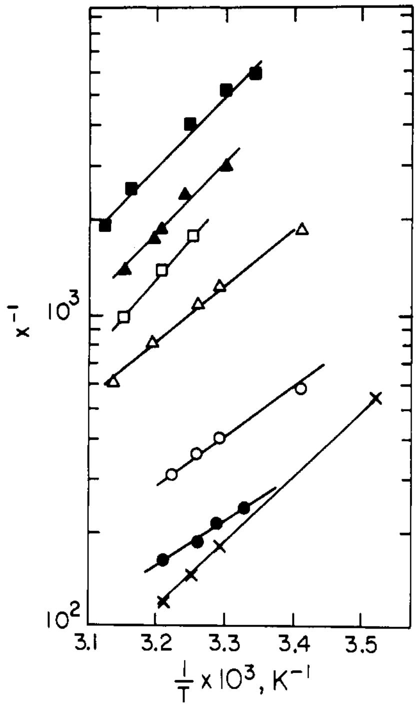

Figure 1. Solubility curves of cholesterol in polar solvents: (×) acetone, (●) ethanol, (○) aqueous ethanol (95%), (△) methanol, (□) aqueous acetone (80%), (▲) aqueous ethanol (80%), and (■) acetonitrile.

where *x* is the mole fraction of the solute and *T* is the absolute temperature in kelvin. The *A* and *B* constants with their corresponding standard deviations, the correlation coefficients, and the prediction standard deviations are given in Tables IV–VI. As the correlation coefficients indicate, the linear expression describes satisfactorily the solubility dependence on temperature, within the given temperature range. The experimental values and the regression lines are shown in Figures 1–3 for

Table IV. Best-Fit Correlation Parameters for Cholesterol Solubilities in Various Solvents

solv	B	β	A	α	r	10^3s
acetone	−4.6426	0.0707	2096.49	21.31	0.9999	5
ethanol	−2.4081	0.0725	1437.84	70.08	0.9983	6
aq ethanol (95%)	−2.0609	1.1699	1415.43	354.18	0.9884	52
methanol	−2.7205	0.2527	1760.55	77.57	0.9968	16
aq acetone (80%)	−5.2548	0.4335	2616.58	234.47	0.9991	17
aq ethanol (80%)	−4.0777	0.4399	2291.19	136.63	0.9952	15
acetonitrile	−3.7444	0.0788	2257.06	24.39	0.9960	4

Table V. Best-Fit Correlation Parameters for Sitosterol Solubilities in Various Solvents

solv	B	β	A	α	r	10^3s
acetone	−1.0147	0.5766	971.00	178.62	0.9252	29
ethanol	−2.8848	0.4036	1630.07	124.73	0.9951	11
aq ethanol (95%)	−2.3166	0.5397	1542.94	166.79	0.9876	15
methanol	−1.3359	0.3864	1441.39	139.25	0.9912	16
aq acetone (80%)	−4.6624	0.9515	2531.96	298.85	0.9869	33
aq ethanol (80%)	−5.4304	0.5055	2813.59	156.54	0.9973	17

Table VI. Best-Fit Correlation Parameters for Cholesteryl Acetate in Various Solvents

solv	B	β	A	α	r	10^3s
acetone	−4.6638	0.6012	1985.37	182.99	0.9956	38
2-propanol	−4.6414	0.5801	2113.45	174.61	0.9865	44
ethanol	−3.3213	0.4973	1901.47	149.46	0.9879	38
methanol	−3.9854	0.6880	2287.20	213.16	0.0016	26
aq acetone (80%)	−5.7930	0.8214	2879.18	254.97	0.9787	30
aq ethanol (80%)	−4.1865	1.3056	2444.47	404.72	0.9731	47

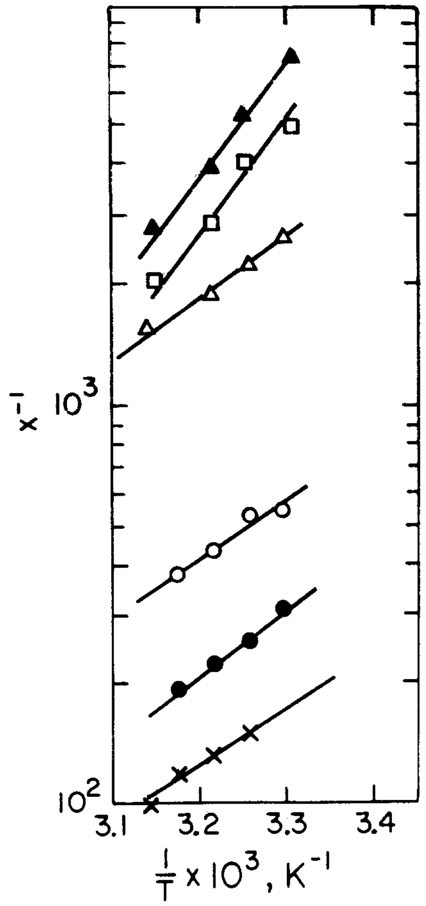

Figure 2. Solubility curves of sitosterol in polar solvents: (×) acetone; (●) ethanol, (○) aqueous ethanol (95%), (△) methanol, (□) aqueous acetone (80%), and (▲) aqueous ethanol (80%).

cholesterol, sitosterol, andd cholesteryl acetate, respectively. The curves of ideal solubilities calculated from (*10*)

$$\log (1/x) = (\Delta H_2^{\mathrm{F}}/2.3R)[1/T - 1/T_{\mathrm{m}}] \qquad (2)$$

are not shown in these figures since they lie much below the experimental ones.

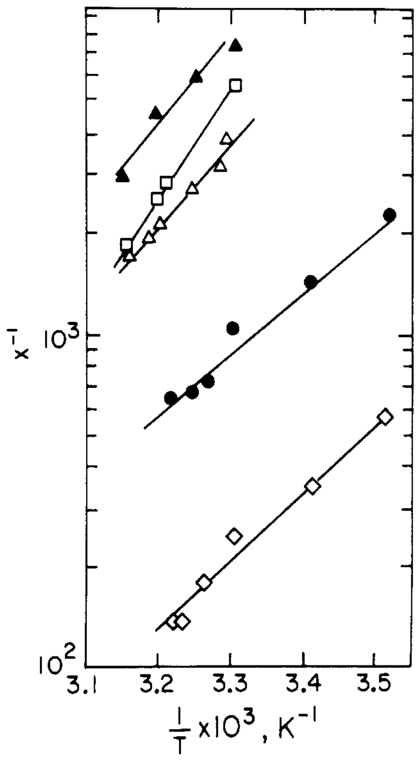

Figure 3. Solubility curves of cholesteryl acetate in polar solvents: (◇) 2-propanol, (●) ethanol, (△) methanol, (□) aqueous acetone (80%), and (▲) aqueous ethanol (80%).

The following conclusions can be drawn from the measured solubility data: (a) all the curves deviate from the ideal solubilities; (b) the solubility of the three steroids increases with temperature; (c) in one steroid, at constant temperature, the solubility decreases with the increasing polarity of the solvent (or the mixture of solvents).

The solutions studied comprise solute–solute interactions (*11*) (dimerization, oligomerization) and solute–solvent and solvent–solvent associations in addition to the crystal–solvate formation (*12*) (hydrate, ethanolate, and methanolate). These factors render the system complex and hardly amenable to a theo-

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retical analysis by modified (*13*) or unmodified regular solution (*10*) or scaled particle theories (*14*). We therefore conclude that the solubility of each steroid is best predicted from the reported best-fit equations.

Registry No. Cholesterol, 57-88-5; sitosterol, 83-46-5; cholesteryl acetate, 604-35-3; methanol, 67-56-1; ethanol, 64-17-5; acetone, 67-64-1; acetonitrile, 75-05-8; 2-propanol, 67-63-0.

Literature Cited

(1) National Heart and Lung Institute Task Force on Arteriosclerosis. "Arteriosclerosis"; National Institutes of Health: Bethesda, MD, June 1971, Department of Health, Education and Welfare Publication No. (NIH) 72-219, Vol. 2.
(2) Small, D. M.; Shipley, G. G. *Science* **1974**, *185*, 222.
(3) Pollak, O. J. *Circulation* **1953**, *7*, 702.
(4) Davis, W. W. *Trans. N.Y. Acad. Sci.* **1955**, *18*, 123.
(5) Garti, N.; Karpuj, L.; Sarig, S. *Cryst. Res. Technol.* **1981**, *16*, 1111.
(6) Mullin, J. W. "Crystallization", 2nd ed.; Butterworth: London, 1965; pp 35-43.
(7) Weichlinz and Marschik. *Biochem. Z.* **1932**, *249*, 312.
(8) Kritchevsky, D.; Tepper, S. A. *Proc. Soc. Biol. Med.* **1964**, *116*, 104.
(9) Stauffer, R. D.; Bischoff, F. *Clin. Chem.* **1966**, *12*, 206.
(10) Hildebrand, J. H.; Scott, R. L. "The Solubility of Nonelectrolytes", 3rd ed.; Dover Publications: New York, 1964; p 272.
(11) Feher, J. J.; Wright, B. D.; McCormick, D. B. *J. Phys. Chem.* **1974**, *78*, 250.
(12) Garti, N.; Karpuj, L.; Sarig, S. *J. Lipid Res.* **1981**, *22*, 785.
(13) Gjaldback, J. Chr.; Niemann, H. *Acta Chem. Scand.* **1958**, *12*, 1015.
(14) Pierotti, R. A. *Chem. Rev.* **1976**, *76*, 717.

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Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous $MnCl_2$, $MnSO_4$, and RbCl at 25 °C

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The osmotic coefficients of aqueous $MnCl_2$, $MnSO_4$, and RbCl have been measured to high concentrations at 25 °C by the isopiestic method. Data for RbCl solutions extend to saturation; data for $MnCl_2$ and $MnSO_4$ extend to supersaturated concentrations. Solubilities were determined for solid $MnCl_2 \cdot nH_2O$ and for RbCl. Results are compared to other activity and solubility data for these salts and, in most cases, the agreement is good. Oxidation of these Mn^{2+} salts was shown to have a negligible effect when care was taken to exclude air, but even without precautions it probably would have been insignificant. Two samples of commercial "99.9%" RbCl were found upon analysis to contain 0.69 and 3.4 mol % impurities, with 64–88% of that amount being potassium. The presence of 1% KCl in RbCl was shown to have a negligible effect on osmotic coefficients below 2.3 mol kg^{-1}, but it lowers them by 0.3% at saturation. Its presence can be accurately corrected for.

Introduction

Activity coefficient data for aqueous electrolyte solutions have numerous applications including solubility, speciation, and other chemical equilibrium calculations. Isopiestic measurements yield accurate solvent activities as a function of concentration, and an integration of these data via the Gibbs–Duhem equation yields solute activity coefficients.

Two sets of isopiestic data have been reported for aqueous $MnSO_4$ at high concentrations (*1*, *2*), but their osmotic coefficients differ by 1.4% at 4.2 mol kg^{-1}. This is a factor of 7–10 times the reproducibility of the isopiestic method (*3*) under favorable conditions. Robinson and Sinclair (*4*) reported isopiestic data for aqueous RbCl from 0.42 to 4.96 mol kg^{-1}, but their data are fairly scattered especially below 1.5 mol kg^{-1}. Robinson later reinvestigated RbCl (*5*) with "purer" material and reported smoothed isopiestic data that are up to 1% higher than his earlier study (*4*). However, Makarov et al.'s high-concentration results (*6*) agree better with the earlier study. Additional isopiestic data for $MnSO_4$ and RbCl are necessary to resolve these significant discrepancies.

Activity data for aqueous $MnCl_2$ are in closer agreement. Three sets of isopiestic data are available, and they agree to 0.5% or better in their overlapping concentration regions (*7*–*9*). However, from 3.59 to 7.70 mol kg^{-1} there are only the 11 points of Robinson (cited in Stokes' Appendix (*8*)), and his point at 4.203 mol kg^{-1} is considerably in error and probably contains a misprint. In addition, they contain three concentration gaps of 0.6 mol kg^{-1} and one of 1.0 mol kg^{-1} in this region. Consequently, additional data are needed to better characterize this salt at high concentrations.

In view of the above considerations, we have made isopiestic measurements at 25 °C for aqueous RbCl to saturation, and for $MnCl_2$ and $MnSO_4$ to supersaturated concentrations.

Experimental Section

The experimental details are nearly identical with those described elsewhere (*3*, *10*). Isopiestic equilibrations were made at 25.00 ± 0.005 °C (IPTS-68), with aqueous NaCl and $CaCl_2$ solutions as reference solutions. Four-day or longer equilibrations were used at the higher concentrations, but this was gradually increased to four weeks by the lowest concentrations. Triplicate samples of $CaCl_2$ solutions were used, and duplicate samples for the other electrolytes. Molalities of each electrolyte at isopiestic equilibrium agreed to better than ±0.1%. All weights were corrected to vacuum.

All isopiestic equilibrations were made in inert cups of tantalum metal. A corrosion test indicated that no significant reaction occurred between $MnCl_2$ and Ta when air was excluded (as occurs during isopiestic equilibrations).

Solutions of NaCl and $CaCl_2$, used as isopiestic standards, have been described elsewhere (*3*). The NaCl stock was analyzed both by dehydration and by AgCl precipitation; $CaCl_2$ was analyzed both by conversion to the anhydrous sulfate and by dehydration (*3*). Molecular masses were 110.986 g mol^{-1} for $CaCl_2$, 136.14 g mol^{-1} for $CaSO_4$, 58.443 g mol^{-1} for NaCl, 125.844 g mol^{-1} for $MnCl_2$, and 150.996 g mol^{-1} for $MnSO_4$.

The $MnCl_2$ stock solution was prepared from filtered Mallinckrodt AR $MnCl_2 \cdot nH_2O$. Direct current arc optical emission spectroscopic analysis (DCAOES) of an evaporated sample detected the presence of only 30 ppm Ca, <20 ppm Si, 3 ppm Mg, and 3 ppm Na by weight. The stock concentration was

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